

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 10.

SEPTEMBER, 1925

No. 9

THE CAUSE OF COLOR IN SMOKY QUARTZ AND AMETHYST*

EDWARD F. HOLDEN, *University of Michigan*

ABSTRACT

The nature of the pigments of smoky quartz and amethyst was investigated from the standpoints of the occurrence and genesis of those minerals, the effect of heat and of radiations upon the colors, the transmission of light, and analysis for the various impurities. It is concluded that amethyst owes its color to a ferric compound, while smoky quartz is probably pigmented by free atomic silicon, liberated through the action of radioactive substances. The literature is discussed as fully as space permits and a chronological bibliography is appended.

I. INTRODUCTION

THE SCOPE OF THIS INVESTIGATION

The causes of the colors of smoky quartz and amethyst have been the subject of numerous investigations, in most of which only one or two methods of inquiry have been pursued. But, any attempt to discover the nature of the pigment of a dilute-colored mineral should be based upon as many different kinds of experimental evidence as possible. The opinion arrived at by a single method of investigation is not to be compared in plausibility to a conclusion substantiated by a number of converging lines of evidence. Therefore the research here described considered the following principal subjects, all of which contribute their share to the final conclusions:

1. The occurrence and genesis of smoky quartz and amethyst.
2. The influence of radiations upon their colors
3. Color changes resulting from heat-treatment of these minerals.
4. The transmission of light through amethyst and smoky quartz.

*From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, June, 1925. That portion of the thesis dealing with the pigment of amethyst was submitted to the Boston Society of Natural History and was awarded the Walker prize for 1925.

5 The nature and amount of the impurities in these varieties of quartz.

A large number of specimens were studied in order that some generalizations, applicable to all occurrences of these minerals, might be made from the results obtained.

The portion of the study devoted to impurities is almost wholly new. Those parts dealing with the transmission of light, the effect of heat upon the colors, and the occurrence and genesis are largely original. However, very little new work on the effect of radiations was carried on, since that field has been very thoroughly covered by other investigators.

HYPOTHESES CONCERNING THE PIGMENTS OF SMOKY QUARTZ AND AMETHYST

Various investigators have suggested that smoky quartz is colored in one or another of the following manners:

a) The pigment is an inorganic compound, probably of trivalent titanium. (15, 16).¹

b) The pigment is a carbon compound. (7, 9, 18, 19, 28).

c) The pigment is a suspension produced by the action of radium radiations. (37, 42).

The ideas which have been advanced as to the cause of the color of amethyst are very similar, and may be classified as follows:

a) The pigment is an inorganic compound.

(1) It is a compound of iron. (2, 6, 11, 20, 22, 34, 56).

(2) It is a compound of manganese. (28, 43).

b) The pigment is a carbon compound. (18, 19).

c) The color is due to the action of radium radiations. (41, 42).

Each of the hypotheses as to the nature of the pigments is discussed in detail in later portions of this paper.

LOCALITIES AND DEPTHS OF COLOR OF THE SPECIMENS STUDIED

The localities and the depths of color of the various specimens of smoky quartz used in this investigation are given in Table I, below. The variation in color is indicated by four color-classes. Class i includes the dark blackish brown specimens, darker than

¹ The numbers in parentheses refer to entries in the bibliography, section X.

² Robert Ridgway. COLOR STANDARDS AND COLOR NOMENCLATURE. Washington, 1912.

Ridgway's² 13''m; class ii, smoky brown, 17'''-13''m; iii, pale grayish brown, lighter than 17'''; and class iv, almost colorless. The order of arrangement within the four classes is not intended to be significant.

TABLE 1. LOCALITIES AND DEPTHS OF COLOR FOR SMOKY QUARTZ

Color-class	Specimen number	Locality
i	1	Pike's Peak, Colorado
	2	Maine
	4	Maine
	6	Pike's Peak, Colorado
	12	Florissant, Colorado
	23	Butt Township, Ontario
	24	Conger Township, Parry Sound district, Ontario
	25	McDonald Mine, Monteagle Township, Hastings County, Ontario
	26	Mining Corporation Claim, Butt Township, Ontario
	27	Lyndock Township, Renfrew County, Ontario
	31	Seffernville, Lunenburg County, Nova Scotia
ii	3	Siberia
	5	Auburn, Maine
	7	Seneca Falls, New York
	8	Unknown
	9	Alexander County, North Carolina
	11	Unknown
	13	Unknown
	14	Unknown
	15	White Mountains, New Hampshire
iii	21	Bedford, New York
	18	Branchville, Connecticut
	28	New Kingston, Pennsylvania
	29	Herkimer County, New York
iv	30	Hot Springs, Arkansas
	10	St. Gothard (?), Switzerland

Table II gives the same data for the specimens of amethyst. Class i includes the dark violet specimens, corresponding to Ridgway's 63'm-63'; class ii, violet, 63'-63'b; iii, pale violet, 63'b-63'e; and class iv, very pale violet, 63'e-colorless.

TABLE II. LOCALITIES AND DEPTHS OF COLOR FOR AMETHYST

Color-class	Specimen number	Locality
i	1	Unknown
	3	Lake Superior district
	4	Unknown
	7	Smithfield, Rhode Island
	14	Uruguay
ii	6	Serra do Mar, Brazil
	13	Genyo, Corea
	17a ¹	Guanajuato, Mexico
	18	Aspen, Colorado
	19	Schemnitz, Hungary
	22	Brazil
iii	23	North Carolina
	5	Iredell County, North Carolina
	8	Jefferson County, Montana
	11	Delaware County, Pennsylvania
	12	Mahatsarakaly, Madagascar
iv	15	Lincoln County, North Carolina
	2	Iredell County, North Carolina
	9	Fujiya, Hoki, Japan
	17b ¹	Guanajuato, Mexico

¹ Specimens 17a and 17b are dark and pale portions of the same group of crystals.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made of the following assistance rendered during this investigation: The Department of Physics of the University of Michigan kindly permitted the use of a photo-spectrometer and of an electroscope for some time, and several members of the staff gave freely of their time and advice. Dr. D. C. Bardwell, of the U. S. Bureau of Mines, radiated several sections of rock crystal. Considerable aid in obtaining specimens was given by Dr. H. V. Ellsworth, of the Canadian Geological Survey; Messrs. M. G. Biernbaum, of Philadelphia, Pennsylvania; W. J. Elwell, Danbury, Connecticut, and W. J. Paquette, Toledo, Ohio; the Philadelphia Academy of Natural Sciences and Ward's Natural Science Establishment, Rochester, New York. Dr. S. C.

Lind, of the U. S. Bureau of Mines, and Professor Waldemar Lindgren, of the Massachusetts Institute of Technology, gave their advice and opinion with regard to certain problems encountered in the work. Professors E. H. Kraus and W. F. Hunt, of the Mineralogical Laboratory of the University of Michigan, kindly supervised the entire investigation and made many indispensable suggestions.

II. PHYSICAL PROPERTIES OF SMOKY QUARTZ AND AMETHYST

Only those properties in which smoky quartz and amethyst differ from ordinary quartz will be considered here.

COLOR—The color of smoky quartz varies from a pale and somewhat yellowish brown (Ridgway's 19'''f), or a pale grayish brown (17'''f), through wood brown (17''') and dark brown (13''m) to black. Amethyst is more constant in hue, ranging from colorless to deep violet (about 63'g to 63'm).

CRYSTAL FORM—Amethyst is nearly always well crystallized, and smoky quartz frequently so, in contrast to the universally massive form of rose quartz.³ Smoky quartz and amethyst were crystallized slowly from aqueous solutions while rose quartz must have formed more quickly from a pasty aqueo-igneous fusion.

The abundant occurrence of trigonal trapezohedrons and bipyramids upon smoky quartz crystals is testified to by numerous citations in the literature. Unequal development of *r* and *z* is also often noted. Amethyst, too, may show these characters. Smoky quartz, and more especially amethyst, are often twinned, the boundaries between the individuals in the twinned crystals being generally sharp and quite regular. Sections of smoky quartz or amethyst crystals are generally free from fractures. These characteristics unite in indicating that smoky quartz and amethyst were formed as the alpha or low-temperature form of quartz. (see part III).

ZONAL COLORING—Both of these varieties of quartz are very often zonally colored. Indeed, amethyst almost always has a zonal distribution of color, which is of two types, frequently combined in a single crystal:

1. In fine lamellae parallel to the rhombohedron faces.
2. A type best revealed by a basal section, which shows a division into sectors. One half of these are violet, and all the other

³ Edw. F. Holden: *Am. Min.*, 9, 77, (1924).

sectors, alternating with those that are violet, are either colorless, yellow, or smoky.

The optical anomalies arising from the intimate twinning of the right and left lamellae and sectors, which correspond to the differently colored areas, are well described and illustrated by Tutton (51, 57). Intergrowths of smoky quartz and amethyst are frequent.

DICHOISM—The absorption of smoky quartz is $e > o$, and the dichroic colors are as follows, depending upon the depth of color:

e	o
slightly brownish yellow	pale pure brown
dark yellowish brown	pure brown
black	very dark brown

The pleochroism of rock crystal which had been colored brown by radium radiations was found to be identical with that of natural smoky quartz.

In amethyst the dichroism is less uniform than in smoky quartz, due to the usual zoning of the colors. The specimens examined showed (1) reddish purple to purple, and (2) purple, bluish purple, or indigo. In some cases no dichroism was apparent. Hailinger (4) made an extensive study of the pleochroism of amethyst, and his results show the absorption to be $e > o$, with the color for e more reddish than that for o .

INDICES OF REFRACTION—The variation of the indices of refraction with the color in quartz has been studied by Forster (7), Dufet (13), Hlawatsch (17), and Wülfing (30). The values which these investigators found for amethyst (ω 1.54418⁴ to 1.54427) lie entirely within the range for rock crystal (ω 1.54418 to 1.54433). The index of an amethyst from Uruguay was increased 5×10^{-5} by heat-decolorization, according to Wülfing. Most of the measurements for smoky quartz agree closely with those of the other two varieties. In the fifteen determinations recorded for smoky quartz the value for ω was between 1.54403 and 1.54436 for thirteen specimens; in the other two cases ω was given as 1.54387 and 1.54388, respectively. Wülfing and Forster found that the heat-decolorization of dark smoky quartz caused no change in the index of refraction, but Hlawatsch noted a slight increase in the fourth decimal place. Even the largest variation in refractivity

⁴ All values of ω are for yellow light.

from one specimen of smoky quartz to another is very slight, rarely attaining a magnitude of several units in the fourth decimal place.

It is unlikely that the pigmenting impurities constitute any large proportion of the total impurities which effect the optical properties of these types of quartz. For this reason it is impossible to draw any plausible conclusions as to the nature of the pigments from this type of evidence.

III. OCCURRENCE AND GENESIS OF SMOKY QUARTZ AND AMETHYST

The production of the characteristic color of such minerals as smoky quartz and amethyst is due to the coexistence of the proper chemical and physical environment in the solutions from which they form. It is necessary that there be present those chemical compounds which constitute the pigment, and it is just as imperative that the mineral crystallizes under favorable physical conditions. Temperature is probably the most important of the physical factors. At this point in the study an effort will be made to determine the chemical and physical conditions prevailing during the formation of smoky quartz and amethyst.

OCCURRENCE

The occurrences of smoky quartz and amethyst may conveniently be classified into the six groups discussed below. With the exception of the last, they are arranged in the most probable order of decreasing temperature and pressure conditions.

1. IN CAVITIES IN DEEP-SEATED IGNEOUS ROCKS, PRINCIPALLY PEGMATITES—Both amethyst and smoky quartz occur frequently in the deep-seated igneous rocks, especially in the drusy cavities of pegmatites. These minerals crystallized out from hot aqueous solutions containing a large amount of carbon dioxide and other mineralizers. Quartz crystals generally coat the walls of the cavities and are among the last differentiates from the magma.

Smoky quartz occurs in a wide variety of pegmatite types, comprising: (a) those with potash feldspar (e.g., Madagascar); (b) gem beryl pegmatites (Mourne Mountains, Ireland); (c) the Li-F-B type, with gem tourmaline and lepidolite (Mount Mica, Maine); (d) the Li-F-Mn-phosphate type (Branchville, Connecticut); (e) the cassiterite and tourmaline pegmatites (Fichtelgebirge); (f) the Cb-Ta-U-rare earth pegmatites, with radioactive minerals (many localities in Ontario).

Smoky quartz is also found in the body of pegmatite veins, where it was often the last constituent to crystallize.

Amethyst is less abundant in pegmatites than smoky quartz and it is not found in the body of the pegmatite veins, but occurs only in the cavities. The drusy cavities containing amethyst and smoky quartz are not confined to pegmatites, though they are most abundant there. Similar pockets often occur in granites, as well as in other deep-seated rocks.

2. IN HYDROTHERMAL VEINS CLOSELY ASSOCIATED WITH GRANITES AND PEGMATITES—These quartz veins were formed by the silica-bearing aqueous solutions which were the last differentiation products of acidic magmas. Amethyst and smoky quartz are sometimes found in cavities in such veins.

3. IN THE ALPINE TYPE OF VEINS—The Alpine veins have been thoroughly studied by Koenigsberger (24, 41, 44). They were formed by hot, ascending waters, rich in CO_2 , which leached out the constituents of the rocks through which they passed. The dissolved substances later crystallized out in new combinations. Naturally, the composition of the minerals thus formed was determined by the nature of the leached rock.

Smoky quartz is abundant in these veins, while amethyst is not infrequent. Smoky quartz is found in the veins in adularia gneiss, biotite gneiss, granites, and acid like rocks, but the quartz in the veins traversing schists of sedimentary origin and basic igneous rocks is almost always colorless. The most important associates of smoky quartz are as follows: (a) *formed before or with the quartz*: adularia; and (b) *formed after the crystallization of the smoky quartz*: fluorite—characteristically red, calcite, the zeolites, and chlorite.

Koenigsberger (24) states that in the central Alps the intensity of color of the smoky quartz crystals depends upon the altitude of the occurrence. He gives the following data for the western part of the protogene:

Up to 1400 m. altitude,	the quartz is colorless
At 1500	a brown color is noticeable
1800	distinct brown color
2300	the typical smoky quartz begins
2900	deep colored morion

Brauns (37) thinks that the color may have been due to radium and that the radium may have been more active at higher levels,

or that a lower temperature in the higher rocks permitted a more intense color to be produced by the radium. Most probably the explanation lies in a temperature effect. If the present altitude of the occurrences represents the proportional depth of the quartz when it was formed, the temperature of the veins now at 1400 m., would at that time have been 45° more than that of the veins now at 2900 m., assuming an added temperature of 1° for each increment of 33 m. in depth. This is a sufficient temperature range to allow the production of the different degrees of color observed (see part V).

Amethyst in the Alps is always accompanied by iron minerals. Limonite is the most frequent associate, others being ankerite, siderite, and chlorite.

4. IN ORE VEINS—Colored quartz is not infrequently found in metalliferous veins. Amethyst occurs in such deposits more often than the smoky quartz. Amethyst has often been noted in the silver veins which Lindgren⁵ describes as “deposits formed near the surface by ascending thermal waters and in genetic connection with igneous rocks.” Examples are the deposits at Schemnitz, Hungary, and Guanajuato, Mexico. It is also noted in the ore-bodies classified as metalliferous deposits formed at intermediate depths,” as, for example, in the lead-silver veins of Příbram, Bohemia, and in the silver veins on the north shore of Lake Superior. Such minerals as the carbonates, the sulfides, barite, and fluorite are common associates of amethyst in ore veins.

When smoky quartz is found in ore veins it is generally in those which are mineralogically related to pegmatites, such as the cassiterite veins of Saxony.

5. IN THE AMYGDALOIDAL CAVITIES OF BASIC IGNEOUS ROCKS—Amethyst is very frequently found in the cavities of basic eruptive rocks. The associated minerals are agate and chalcedony, formed earlier than the amethyst; and datolite, prehnite, pectolite, apophyllite, the zeolites, and calcite, formed later. In some localities it seems evident that these minerals were precipitated from magmatic liquids in the gas cavities of cooling lavas; in others they were formed by the action of atmospheric waters percolating through recently erupted lava flows.

⁵ Waldemar Lindgren: MINERAL DEPOSITS, 2nd edition, 465 *et seq.* 1919.

Amethyst is found in veins and geodes in the Triassic traps of New Jersey, the Connecticut Valley, and Nova Scotia. Smoky quartz is only occasionally noted in these rocks. Another well-known occurrence for amethyst is in the chalcedony and agate geodes from melaphyres in Brazil and Uruguay.

6. RELATIVELY UNIMPORTANT MISCELLANEOUS OCCURRENCES—A few occurrences of amethyst and smoky quartz in calcareous rocks, sandstones, and quartzites, in which there was no known genetic connection with igneous rocks, have been reported. In these instances the quartz crystals must have been deposited by waters of only moderate warmth. Amethyst often occurs in the agatized trees of Yellowstone Park and Arizona, the silicification having been caused by cool waters of meteoric origin.

ELEMENTS ASSOCIATED WITH SMOKY QUARTZ AND AMETHYST

Many other elements occur in the silica-bearing solutions from which these varieties of quartz crystallize. Minerals containing the following elements are frequently found with both smoky quartz and amethyst: H, as water; C, as CO₂, very common both as a gas and in carbonates; Na, K, Ca, Mg, Fe, Mn, Al, and Si in the aluminosilicates and so forth; F, in fluorite, apatite, apophyllite, and topaz; B, in tourmaline and datolite; and Ti in the always present rutile inclusions, and as anatase and brookite.

Many of the rarer elements are more characteristically associated with smoky quartz than with amethyst. These include: the less common alkalis, Li, Rb, and Cs, in lepidolite, tourmaline, alkali beryl, and spodumene; Be, in beryl; P, in apatite and other phosphates; Sn, in cassiterite; W, in wolframite; Mo, in molybdenite; and in the numerous rare earth and radioactive minerals: Cb, Ta, Th, U, Ra, the rare earths, and Zr.

The frequent occurrence of smoky quartz in association with rare earth and radioactive minerals is very significant, for later it will be indicated that smoky quartz may have been colored through the action of radioactive elements. In Ontario smoky quartz is a constant associate of radioactive minerals,⁶ and the same association is frequent in Madagascar.⁷ Enormous smoky quartz crystals occur in the well known radioactive pegmatite of Baringer Hill, Texas.

⁶ H. V. Ellsworth: *Summ. Rept. Geol. Surv. Canada* 1921, pt. D, 51-70.

⁷ A. Lacroix: *MINÉRALOGIE DE MADAGASCAR*, II, 260 (1922).

Only very pale varieties occur elsewhere than in acid igneous rocks, which are much more radioactive than other types of rocks.⁸ There is, therefore, a correlation between the occurrence of smoky quartz and the radium content of the rocks in which it is found.

Amethyst is often accompanied by minerals of some elements rarely found with smoky quartz: S, As, Cu, Zn, Pb, Ag, and Au, in the sulfides, sulfo-salts, and native metals; Ba, in barite; the compounds of Fe, limonite, goethite, hematite, and siderite, which are the most characteristic associates of amethyst, especially the darker varieties. One of these iron minerals invariably accompanies amethyst in the Alps (24, 41, 44). Amethyst is associated with limonite veins in Lincoln County, North Carolina. It occurs on siderite at Macskamező in the Siebenbürgen, and on carnelian containing 3 per cent Fe_2O_3 in the "Buntsandstein" of Waldshut, Baden. At Hüttenberg, Carinthia, it is found as druses on siderite and limonite. Near Onega-See, Russia, amethyst enclosing goethite needles is found.

A specimen from El Paso County, Colorado, was zoned in smoky brown and violet. There were a few scattered needles of goethite in the smoky area, but the violet portions are literally crowded with them.

In the Lake Superior district much of the amethyst has inclusions of hematite or goethite. In specimens examined the color was deepest for several mm. below the thin layer of hematite inclusions, the rest of the crystal being white or colorless. These relations indicate that the violet quartz began to be formed when a sufficient concentration of iron was attained in the mineral solutions, the quartz previously formed being colorless. As the amount of iron increased the color became darker, and finally the deposition of hematite took place. In Madagascar (49) also, red and black hematite inclusions occur in amethyst.

Many more instances of the occurrence of iron minerals with amethyst might be cited. It is significant that the amethyst from amygdules in basic igneous rocks is usually very dark, while that in pegmatites and related veins is most apt to be pale. Basic igneous rocks are high in iron; acid rocks are low.

While many elements occur in the solutions from which amethyst has been deposited, iron is the only pigmenting substance which is characteristically present. The facts presented in the preceding paragraphs are good evidence that iron is essential in

⁸ Cf. *U. S. G. S. Prof. Paper* 121, 54-57 (1921).

producing the color, a conclusion which data given later will substantiate.

The chemical factors necessary in the formation of smoky quartz and amethyst, aside from the presence of the compounds causing the colors, are a moderate amount of uncombined silica in the aqueous solution, with considerable carbon dioxide and other mineralizers. With too great a concentration of silica the cryptocrystalline or poorly crystallized varieties of quartz are likely to be formed. At temperatures within the formation range of opal, the presence of carbon dioxide seems to favor the growth of quartz instead of opal.⁹

PARAGENESIS

The paragenetic relationships of smoky quartz, amethyst, and the more important associated minerals are shown in Table III. Very little additional discussion is necessary. These varieties of quartz were generally formed after the colorless or white quartz of the pegmatites in which they occur, and after the chalcedony and agate of basic rocks. In the first instance, this is due to the temperature, which at first is too high to allow the pigmentation of the quartz. In the basic rocks, the cryptocrystalline varieties are at first precipitated from the concentrated silica solutions, to be followed later by the more slowly formed crystals.

TABLE III. PARAGENESIS OF SMOKY QUARTZ AND AMETHYST

	Time of formation relative to that of smoky quartz and amethyst		
	Before	Same time	Afterwards
Orthoclase, microcline, albite	X	X	
Adularia	x	X	
Tourmaline, beryl, micas	X		
Rare earth minerals	X		
Apatite	X	x	
Rutile, anatase, brookite	X	X	x
Hematite, limonite, goethite	x	X	X
Calcite, chlorite		x	X
Zeclites, apophyllite, pectolite		x	X
Fluorite			X
Colorless or white quartz	X	x	x
Agate and chalcedony	X	x	x

X indicates "generally"

x indicates "occasionally"

⁹ C. Doelter: HANDBUCH DER MINERALCHEMIE, II, 153-157 (1914).

TEMPERATURE OF FORMATION

The minimum temperatures at which decolorization occurs is shown in part V to be approximately 225° for smoky quartz and 260° for amethyst. It will be of interest to ascertain whether other lines of evidence unite in indicating a formation temperature below the point of decolorization.

CRYSTALLOGRAPHIC EVIDENCE—Wright and Larsen¹⁰ have indicated criteria which may be used to distinguish quartz formed above 575° from quartz formed below that temperature. As shown by the description of the physical properties in section II, the application of these criteria to smoky quartz and amethyst prove unquestionably that they were formed below 575°, as the alpha modification of quartz.

EVIDENCE FROM LIQUID AND GASEOUS INCLUSIONS—Quite precise information concerning the temperature and pressure conditions during the formation of smoky quartz and amethyst is afforded by the abundant liquid-gas-filled cavities.

From an extensive study of artificial and natural crystals, Sorby¹¹ concluded that "at the temperature at which they were formed, the fluid cavities in crystals are full of fluid, and . . . at a lower temperature they contain vacuities, owing to the contraction of the fluid on cooling. . . . The temperature (of formation) . . . might be ascertained by determining what increase of heat would be required to expand the fluid so as to fill the cavities."

Much more recently, Johnsen (47) by the application of accepted physico-chemical relations, has been able to construct a temperature-pressure curve, at some point along which an amethyst crystal studied by him must have been formed. This crystal contained a cavity filled with CO₂. At 20° both liquid and gaseous phases of CO₂ were present in the ratio of 70 to 30 by volume, respectively. At 30°, approximately the critical temperature of CO₂, the whole inclusion became gaseous. From the volume ratios of the two phases at 20° and their known densities¹² Johnsen calculated the density of the originally included CO₂ gas to be 0.60. Using van der Waal's equation, he then calculated the pressure-temperature curve along which carbon dioxide would have that specific gravity. (This is the curve *ab* of Figure 2 in this

¹⁰ F. E. Wright and E. S. Larsen: *Am. J. Sci.*, **27**, 421-447 (1909).

¹¹ H. C. Sorby. *Quart. J. Geol. Soc.*, **14**, 453-500 (1858).

¹² E. H. Amagat: *Compt. Rend.*, **114**, 1093-1098 (1892).

paper). The amethyst crystal in question must undoubtedly have formed at a temperature and pressure falling at some point on the curve, but one quantity must be known if the other is to be found.

It appeared that both the temperature and pressure under which a specimen of quartz was formed could be approximately determined if the mineral contained both water and carbon dioxide inclusions. Examination of a series of crystals showed that such is not infrequently the case. These gaseous and liquid inclusions may be classified into three types, as follows:

1) INCLUSIONS CONSISTING OF WATER ALONE, OR OF AN AQUEOUS SOLUTION, BUT WITH NO FREE CARBON DIOXIDE—Such cavities contain small contraction bubbles, due to the cooling of the liquid from its temperature when enclosed in the growing quartz crystal. The temperature at which the bubble just disappeared

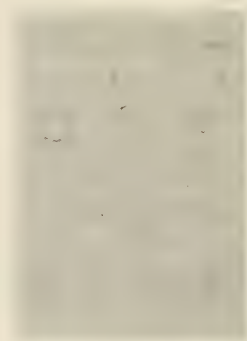


FIG. 1

was determined. This is practically equal to the formation temperature, for the slight effect of pressure may be disregarded.

The fragment of quartz under examination was placed in a bath of melted paraffine, contained in a crystallizing dish on a microscope stage. The temperature of the bath, measured with a mercury thermometer, was gradually increased by means of a current passed through a small platinum resistance coil immersed in the liquid. The temperature at which a bubble in a cavity just vanished could thus be readily determined.

In Fig. 1, sketches *a*, *b*, *c*, and *d*, made at room temperature, illustrate this first type of inclusion. In *a* and *b*, from smoky quartz No. 14, the bubbles disappeared at $205 \pm 5^\circ$; in *c* and *d*, from amethyst No. 9, at $240 \pm 10^\circ$. Negative crystal cavities are illustrated by *b* and *d*.

2) INCLUSIONS CONSISTING ENTIRELY OF CARBON DIOXIDE—Below the critical temperature, 31° , these frequently contain both the liquid and gaseous phases. Following Johnsen's method it is possible to construct a pressure-temperature curve, passing through the point at which the specimen must have formed. In Figure 2 are given the pressure-temperature curves for several densities of CO_2 .

Sketches *g* and *h*, Figure 1, from fragments of amethyst Nos. 12 and 11, respectively, illustrate inclusions entirely of CO_2 . The inner bubble is gaseous, the outer zone liquid CO_2 . The sketches show the conditions at room temperature. Above 31° there is only one phase, gaseous CO_2 .

3) INCLUSIONS OF WATER WITH BUBBLES OF CARBON DIOXIDE AND WATER VAPOR—The CO_2 in the cavity exceeds the amount soluble in water. Below 31° it may be either entirely gaseous CO_2 or may exist as two phases. These CO_2 bubbles in water furnish the same kind of information as is given by those inclusions entirely of CO_2 .

The carbon dioxide bubbles can be distinguished from the contraction bubbles since the ratio of CO_2 bubble to liquid is quite variable from one cavity to another in a single fragment, while in bubbles due solely to contraction the relation is necessarily quite constant. Undoubtedly, the CO_2 in this third type must have been enclosed in the quartz as bubbles in the water.

Bubbles of CO_2 in water are illustrated by diagrams *e* and *f* (smoky quartz No. 15) and by *i*, a negative crystal cavity (smoky quartz No. 4). In the cavities represented here the density of the CO_2 is such that it all remains gaseous at room temperature.

When the first together with either the second or third types of inclusions occur in the same specimen, both the temperature and pressure at the time of formation are easily determinable. The water inclusions give evidence as to the temperature, which enables the pressure to be determined from the temperature-pressure curves afforded by the CO_2 inclusions. The temperature determination is the more accurate because it involves no calculation.

The cavities sketched in *j* and *l*, Figure 1, at 25° are of the first and third types, respectively, and they occurred in the same crystal (smoky quartz No. 5). The contraction bubble in *j* disappears at $135 \pm ^{\circ}$. Sketches *k* and *l* are of the same cavity at

different temperatures. In *k*, the temperature is greater than 31°, when all the CO₂ is gaseous. In *l* the innermost zone is a globule of liquid CO₂ at the interface between the gaseous CO₂ and the outermost zone of water.¹³

In the table given below are tabulated the results of examining a number of specimens of amethyst and smoky quartz in this way.

TABLE IV. TEMPERATURE (*t*) AND PRESSURE (*p*) OF FORMATION OF SMOKY QUARTZ AND AMETHYST AS DETERMINED FROM THEIR LIQUID AND GASEOUS INCLUSIONS

SMOKY QUARTZ			AMETHYST		
Spec. no.	<i>t</i>	<i>p</i>	Spec. no.	<i>t</i>	<i>p</i>
— ¹	110 <i>ca.</i>	—	1	97 ± 2°	—
10	100?	< 100 atm.	14	135 ± 1	—
29	110 ± 5	—	— ¹	140 ± 5	—
18 ²	125 ± 5	—	23	140 ± 3	—
4	125 ± 10	100	2	150 ?	600 ± 50 atm.
12	135 ± 5	—	15	185 ± 10	—
5	135 ± 5	175 ± 25	— ²	210 ± 10	—
30	135 ± 5	—	9	240 ± 10	—
1	140 ± 10	—	12	—	Up to 250 ⁴ to 300 ⁵ <i>ca.</i>
7	180 ± 10	—	11	—	450 ⁴ to 550 ⁵ <i>ca.</i>
3	205 ± 5	—	— ³	—	450 ⁴ to 550 ⁵ <i>ca.</i>
14	205 ± 5	—			
— ³	225	—			
2	—	< 100			
15	—	< 100			

¹ Smoky gray crystals in a water-filled geode, Uruguay. C. W. Gumbel, *Sitzb. k. Bayr. Akad. Wiss., Math.-phys. Cl.*, **10**, 241-254 (1880).

² G. W. Hawes, *Am. J. Sci.*, **21**, 203-209 (1881) also has studied crystals from this locality. From his data the writer finds: *t* 110-114°, *p* up to 500 atm.?

³ Smoky quartz from Alpligengletscher. J. Koenigsberger, *Neues Jahrb Mineral. Geol., Beil.-Bd.*, **14**, 43-119 (1901).

¹ A cut gem, locality unknown.

² Very pale crystal from Schemnitz, with a macroscopic bubble.

³ Mursinka, Johnsen, *loc. cit.*

⁴ Assuming *t* < 150°

⁵ Assuming *t* = 200°

¹³ G. W. Hawes. *Am. J. Sci.*, **21**, 203-209 (1881) describes an interesting series of three-zoned CO₂ and water inclusions in smoky quartz from Branchville, Connecticut.

Figure 2 illustrates the paragenesis of smoky quartz, amethyst, and carbon dioxide. It is based on Johnsen's work, with adaptations and much added data. The normal geothermobar, as shown, is that for a temperature increase of 1° per 33.3 m. increase in depth, and a pressure rise of 1 atm. per 4 m. The depths in the earth's crust are indicated at intervals of 2 km along this curve. The pressure-temperature curves for several densities of CO_2 are given. To the right of these curves the corresponding proportion of liquid CO_2 existing at 20° is indicated, in terms of its volume percentage of the whole inclusion of CO_2 . The vapor pressure-temperature curve for water is also given.

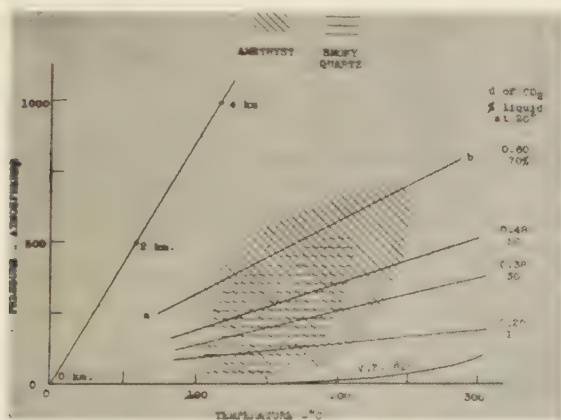


FIG. 2

The probable pressure-temperature conditions under which amethyst forms are represented by the area which is obliquely ruled, while the hypothetical region of formation of smoky quartz is shown by horizontal lines. It is obvious that amethyst is formed under a greater temperature and pressure range, both higher and lower, than smoky quartz, and that the two types may form simultaneously through a considerable variation in temperature and pressure, as frequently happens.

The diagram (Fig. 2) shows that both of these varieties of quartz were formed under either lower pressure or higher temperature than normal for the earth's crust, or under both lower pressure and higher temperature. The latter is most probable. Those are the conditions to be expected in pockets containing hot aqueous solutions. The open cavities relieve their contents

of the normal pressure, while the solution is hotter than the normal temperature because of its magmatic origin. The actual pressure must be that of the water vapor and gases. The pressure is shown by the inclusions to exceed that which would be caused by the water vapor alone at the several temperatures.

EVIDENCE FROM PARAGENESIS—In respect to the formation temperature, the paragenetic relationships of these two colored varieties of quartz agree with the evidence from the inclusions. Adularia, formed before or with the earlier-formed crystals of smoky quartz, is frequently deposited by waters of 50-150° in temperature, according to Lindgren.¹⁴ Doelter¹⁵ concludes that orthoclase may have formed at temperatures as low as 100°. Both albite and orthoclase have been found in sedimentary rocks under circumstances positively demonstrating their formation after sedimentation.¹⁶ Muscovite, also of an earlier stage than smoky quartz, has been synthesized at 196-233°. Therefore, the lowest possible formation temperature for these earlier-crystallized minerals lies well below the highest possible temperature of formation for smoky quartz and amethyst, as indicated by the inclusions and the decolorization experiments.

Calcite, fluorite, and chlorite, minerals of a later stage than smoky quartz and amethyst, are capable of formation through a rather wide range, down to very low temperatures. The zeolites are stable in a more restricted region and are characteristically low temperature minerals. They have been synthesized at temperatures as low as 100°, and in nature have been formed at even lower temperatures. Phillipsite, for example, is found in deep sea muds. The zeolites, fluorite, calcite, and chlorite could well have been formed below the lowest temperatures indicated for smoky quartz and amethyst.

SUMMARY

It is shown that amethyst and smoky quartz were crystallized from hot aqueous solutions in cavities, under less pressure than normal for the depth at which they were formed, and in a temperature range of about 110-220° for smoky quartz, and 90-250° for amethyst. The crystals grew rather slowly, from not too highly

¹⁴ Waldemar Lindgren: *MINERAL DEPOSITS*, 2nd edition, 468 (1919).

¹⁵ C. DOELTER: *HANDBUCH DER MINERALCHEMIE*, II, pt. 2, 555 (1917).

¹⁶ R. A. Daly: *Proc. Nat. Acad. Sci.*, 3, 659-665 (1917).

concentrated solutions. These solutions contained many other compounds than silica, notably carbon dioxide and other mineralizers. Smoky quartz is frequently accompanied by radioactive minerals. The iron minerals, hematite, limonite, goethite, and siderite are generally found with amethyst.

IV. RADIATIONS AND THE COLOR OF SMOKY QUARTZ AND AMETHYST

Much has been published concerning the effects of radiations on the color of smoky quartz and amethyst [Doelter (32, 33, 38, 39, 40, 42, 53), Egoroff (27), M. Berthelot (28), Miethe (29), D. Berthelot (31), Phillips (35), Simon (36), Brauns (36), Newberry and Lupton (45), Meyer and Přibram (50), and Lind and Bardwell (54)] For the present investigation Dr. Bardwell kindly exposed three sections of New York rock crystal to the penetrating radiations from 230 mgs. Ra. for 112 days. The dichroism and absorption spectrum of these artificially colored specimens were found to be identical with that of the natural smoky quartz (see sections II and VI).

The many investigations which have been reported by various workers allow very general conclusions to be made:

a) The color of heat-decolorized amethyst and smoky quartz is restored by the penetrating radiations from radium.

b) Pale specimens may have their colors intensified in the same way, but sometimes amethyst becomes brown on radiation.

c) Colorless quartz normally becomes smoky brown, but sometimes is rather resistant to coloration by radium, and rarely becomes violet.

d) A zonal coloring like that observed in naturally colored quartz crystals is sometimes produced by radiation.

e) The radium-induced colors are unstable at moderate temperatures, and radiated specimens usually phosphoresce when heated.

RELATION BETWEEN RADIUM RADIATIONS AND THE PIGMENTS OF SMOKY QUARTZ AND AMETHYST

There is good evidence that the smoky brown color produced by the radiation of rock crystal is identical with the coloration of natural smoky quartz. The artificially colored variety agrees exactly with the natural in hue, dichroism, and absorption spec-

trum. Furthermore, the zonal coloring observed in natural crystals is often duplicated in the radiated rock crystal. Both artificial and natural smoky quartz are decolorized at moderate temperatures. These facts suggest that the pigmentation of natural smoky quartz is due to the radiation of colorless quartz by radioactive substances in the solutions from which it formed. This hypothesis will be further supported and elaborated.

On the other hand, it does not seem possible to trace any inevitable connection between the action of radium and the natural production of the amethystine color. Radiation of almost any specimen of quartz, such as rock crystal, or rose quartz, or frequently even amethyst itself, brings about the brown coloration. On the contrary, the violet color is very rarely produced except when the color of pale or heated amethyst is deepened by radiation. The color of amethyst must be due to some characteristic pigmentation impurity, which other parts of the present study indicate to be a ferric compound.

HYPOTHESES PROPOSED TO ACCOUNT FOR THE COLORATION OF MINERALS BY RADIATIONS

The explanations which have been advanced to account for the production of color by the radiation of a mineral fall into two main classes:

1. The color is due to the formation of colloidal particles.
2. The color is due to the liberation of electrons without the production of colloidal particles.

Doelter (40, 42), especially, has supported the first view. According to his view colorations are probably due to the formation of colloidal particles by the disintegration of impurities or of the pure mineral substance itself. The size and degree of dispersion of the resulting particles would determine the color produced, as in any other colloidal solution. Doelter suggests colloidal sodium or lithium, derived from included silicates, as the pigments in smoky quartz and amethyst. Decolorization by heating would be due to a change in the size of the particles or of their dispersity. Wild and Liesegang (52) have pointed out that it is very difficult to accept the hypothesis that solid colloidal particles might migrate through the rigid crystalline framework of a mineral.

Lind and Bardwell (54) have recently proposed a theory which seems much more probable: Certain groups of electrons are

thrown into metastable positions by the radiations. No displacement of the atom is involved, nor are any colloidal particles produced. Their assumption is that the displaced electrons are able to vibrate with a frequency which may fall in the visible region, causing the production of a color. They may return to their normal positions under the influence of heat.

SCATTERING OF LIGHT BY SMOKY QUARTZ AND AMETHYST

Strutt (46) has observed that a ray of light passing through a section of smoky quartz is strongly scattered, the path of the light being visible. In clear, colorless quartz, however, there was no scattering. Raman (48) has made similar observations.

Vanzetti (55, 58) found the light-scattering in morion to be pronounced. After decolorization of the section at 300° the path of the light ray was no longer visible. In a zonally banded section light was scattered by the brown bands, but not by those which were colorless. Vanzetti concluded that it was plausible to suppose that the light-scattering and the color, both destroyed by heating and restored by radiation, were due to a colloidal suspension whose particles might vary in size. Perhaps a partial decomposition of the SiO_2 was involved.

Some observations made during the present study verify Vanzetti's experiments on smoky quartz. The scattering of light from quartz was found to be of three types:

1. From microscopically visible cavities and inclusions. Common to all quartz, and unaffected by heat.
2. From long narrow areas of scattering particles. Noticeable in rock crystal as well as in smoky quartz. Neither of these first two types concern the color.
3. The third type of light-scattering has a connection with the color. It is impossible to detect any microscopically visible particles which could be responsible for this effect. There is a general scattering in the entire path of the beam. In the following paragraph only this type is considered.

Eight specimens of smoky quartz were examined for this phenomenon. The effect was decidedly stronger in the darker specimens. From each of two specimens of smoky quartz (Nos. 6 and 8) pairs of sections were cut from single crystals. One section of each pair was decolorized by long and gentle heating, while the other was reserved for comparison. In both cases the original section scattered light strongly while the decolorized section

showed little or no scattering. It is very evident, then, that the coloration of smoky quartz is to be correlated with the scattering of light by microscopically invisible particles, which were probably produced by the action of radioactive substances.

It seems probable that the particles are of atomic rather than colloidal size. There are great difficulties to be met in explaining the migration, agglomeration, and dispersion of colloidal particles in a crystalline structure. As shown by evidence to be given later the pigmenting and light-scattering particles may well be atoms of elemental silicon.

In seven amethyst specimens there was no light-scattering, which is further evidence opposed to coloration by colloidal alkalies, the theory which has been proposed by Doelter (40, 42).

SUMMARY

The evidence given thus far is in agreement with the theory that smoky quartz owes its color to atoms of silicon, formed by the disintegration of silica, through the action of radium radiations. The mechanism of the formation of the free silicon may perhaps be pictured in this way: The radiations may remove the four outer electrons from a silicon atom, which would then be equally shared by the two associated oxygen atoms. As a result, two free oxygen atoms and a free silicon atom would be formed. They could take no part in the crystal structure since their attractive force for other atoms would have been destroyed. Hence, they should act as small inclusions, the silicon atoms producing the light-scattering and the color so characteristic of smoky quartz. We would expect the silicon atoms to be most effective in scattering light because of their greater atomic weight, and the possibility of the escape of the oxygen atoms.

V. THE COLOR CHANGES CAUSED BY HEATING

Several investigators have made rather detailed studies of the heat-decolorization of smoky quartz and amethyst. The usual method of study has been to gradually increase the temperature, noting the points at which the various changes in color occur. But, with longer heating at a constant temperature, the decolorization takes place at a lower temperature than that given by the first method. Therefore it was thought desirable to more thoroughly investigate the influence of long-continued heating upon the

decolorization. This new data, combined with the large number of observations reported by other investigators, affords, quite a complete knowledge of the effect of heat upon the colors of smoky quartz, and amethyst.

REVIEW OF THE LITERATURE

Simon (36) and Herman (34) have investigated the decolorization of these minerals in various reducing and oxidizing atmospheres. They found that the surrounding gas had no influence on the color changes in smoky quartz and amethyst.

Simon worked with a large number of specimens and heated them both in hydrogen and oxygen. In smoky quartz the first change was to a smoky- or greenish-gray. The mineral began to be decolorized at 300° and decolorization was complete at $330-370^{\circ}$ in less than an hour. Heating for 48 hours at 290° also caused complete loss of color. With amethyst there were several distinct color changes as the temperature was increased. At $170-210^{\circ}$ the specimens became gray violet. The change to colorless began at about 300° and was complete at 400 to 500° . A yellow coloration frequently superseded the colorless stage, and finally, above 700° , the specimens became milky white.

Hermann (34) heated specimens of smoky quartz and amethyst at about 700° for two hours in the following atmospheres: air, oxygen, illuminating gas, sulfur vapor, hydrogen, nitrogen, ammonium chloride vapor, and ammonia gas. The color of all amethyst specimens changed from the original hue through gray-violet and yellow stages to opalescence. All the fragments of smoky quartz became colorless and clear.

Wild and Liesegang (56) have recently investigated amethyst. All of the specimens became colorless by 500° , and on further heating became milky. The darker specimens often became smoky yellow, while the paler ones changed to clear yellow. One specimen, studied in detail and heated in air, began to be decolorized at $180-200^{\circ}$, was completely colorless at 340° , and became pale yellow at 350° .

Less detailed work has been done by other investigators. Heintz (6) decolorized a specimen of dark amethyst at 250° . Berthelot (28) found the decolorization temperature of an amethyst to be 300° . The color of deep black morion was lost at 290° , according to Forster (7). Koenigsberger (21) found the decolorization tem-

perature of smoky quartz from several localities to be 295° after six to seven hours, and 370° after several minutes of heating. He also completely decolorized a specimen of smoky quartz in a bomb at 400° and 400 atmospheres pressure.

NEW OBSERVATIONS

In the measurements made at 235 ± 10^{17} and at $240 \pm 10^{\circ}$ the fragments of quartz, from one to three cm. in diameter, were heated on an electric hot plate in a pyrex flask. A thermometer was inserted through the pierced cork, its bulb being placed beside the fragments. For the determinations at higher temperatures, a small electric oven was constructed. The temperatures were measured by means of a mercury thermometer.

TABLE V. HEAT-DECOLORIZATION OF SMOKY QUARTZ

Explanation of table.—At each different temperature (i.e. 235° , 275° , etc.) new specimens were taken. The colors are given in Ridgway's terms, and they are also designated by less exact but more readily understood terms. The colors were determined both when the specimens were hot and after they had cooled to room temperature.

Temp. during heating	Time of heating	Total time of heating	Color noted at:	Resulting color	
				Specimen No. 8	Specimen No. 6
Original color			20°	13''1; medium dark brown	13''n; very dark brown
$235 \pm 10^{\circ}$	3 hrs.	3 hrs.	235 20	Paler; yellowish-greenish As originally	Paler; dark greenish brown As originally
235 ± 10	19 hrs. more	22 hrs.	235 20	25'''g; pale greenish yellow 15'''d; pale brown	21'''1; dark greenish brown 13''m; dark brown
235 ± 10	15 hrs. more	37 hrs.	235 20	Practically colorless; yellowish Practically colorless; faintly brownish	19'''i; greenish brown 13''m; dark brown
235 ± 10	21 hrs. more	58 hrs.	235 20	As above As above	19'''j; greenish brown 15'''j; medium dark brown
235 ± 10	23 hrs. more	81 hrs.	235 20	As above, has become stable 15'''a; medium brown
235 ± 10	69 hrs. more	150 hrs.	235 20	21'''g; almost colorless 15'''a-b; medium brown, has become stable

¹⁷ The temperatures given in this section have all been corrected for the exposed column of mercury in the thermometer.

TABLE V (continued)

Temp. during heating	Time of heating	Total time of heating	Color noted at:	Resulting color	
				Specimen No. 8	Specimen No. 6
275±5	3 hrs.	3 hrs.	275 20	Very pale greenish yellow 15'''c; pale brown	
275±5	2 hrs. more	5 hrs.	275 20	Almost colorless Practically colorless; faint trace of brown	
275±5	8 hrs.	8 hrs.	275 20		21'''j; deep grayish olive 15'''k; medium dark brown
275±5	23 hrs. more	31 hrs.	275 20		Almost colorless; slightly green 15'''c; pale brown
310±5	1 hr.	1 hr.	310 20	Almost colorless; slightly greenish 15'''e; pale brown	21'''a; greenish brown 15'''k; medium dark brown
310±5	2 hrs. more	3 hrs.	20	Practically colorless; slightly brownish	15'''c; pale brown
380±5	6 mins.	6 mins.	380 20	Almost entirely colorless	
380±5	18 mins.	18 mins.	380 20		Greenish yellow Pale brown
380±5	12 mins. more	30 mins.	380 20		Greenish yellow 19'''f-g; very pale yellowish brown
420 ca	6 mins.	6 mins.	400 20		Entirely colorless

TABLE VI. HEAT-DECOLORIZATION OF AMETHYST

Temp. during heating	Time of heating	Total time of heating	Color noted at:	Resulting color		
				Specimen No. 6	Specimen No. 8	Specimen No. 9
Original color			20°	63'; medium vt.	64'b; medium pale vt.	64'e; pale vt.
235±10°	16 hrs.	16 hrs.	235	62''f; pale gray vt.	60''e; pale gray vt.	59''f; pale gray vt.
			20	64'b; medium pale vt.	As originally	As originally
235±10	66 hrs. more	82 hrs.	235	59''f; pale gray vt.	60''e; pale gray vt.	59''f; pale gray vt.
			20	65'd; pale vt.	As originally	As originally

TABLE VI (continued)

Temp. during heating	Time of heating	Total time of heating	Color noted at:	Resulting color		
				Specimen No. 6	Specimen No. 8	Specimen No. 9
315±7	4 hrs.	4 hrs.	315 20		Pale gray vt. As originally	Pale gray vt. As originally
315±7	45 hrs. more	49 hrs.	315 20		57'''g; very pale gray vt. 64'd-e; pale vt.	Practically color- less 64'g-; very pale vt.
305±5	22 hrs. more	71 hrs.	305 20		Practically colorless 64'd-e; pale vt.	Practically colorless 64'g-; very pale vt.
385±20	1½ hrs.	1½ hrs.	385 20		Colorless 65'f; pale vt.	Colorless Colorless
420 ca.	2 hrs. more	3½ hrs.	420 20		Colorless Colorless	
				Specimen No. 6	Specimen No. 5	Specimen No. 4
Original	color			63'; medium vt.	64'c; medium pale vt.	64'm; dark vt.
420 ca.	½ hr.	½ hr.	20	21'''e; pale olive buff		
420+	2 hrs. more	3½ hrs.	420+ 20	16'j; orange brown Same as hot	White, translucent Same as hot	Colorless to white Same as hot

The decolorization of smoky quartz is plainly a time-temperature reaction. At 380-420° the decolorization is complete and immediate. Rapidly increasing time is required to discharge the color as the temperature of heating is lowered. Sometimes there is a tendency for the decolorization at low temperatures to be more or less incomplete, as in the case of specimen No. 6. The almost black original color is completely discharged at 420°, but at lower temperatures, no matter how long the heating is continued, an increasingly greater residue of the color remains. After being heated for eighty-one hours at 235±10°, the color was a medium brown, which did not change after a further exposure of sixty-nine hours at the same temperature, but the paler specimen No. 8 was brought to practically complete decolorization at that temperature. The size of the fragments is also a factor in the decolorization of smoky quartz.

The following table shows the time necessary for complete decolorization of smoky quartz at various temperatures, or for attaining a pale but stable color.

TABLE VII. TIME NECESSARY FOR DECOLORIZING SMOKY QUARTZ AT DIFFERENT TEMPERATURES

Temperature	Time necessary	Observer
420°	Almost immediate	Holden; specimen No. 6
380	Almost immediate	Holden; No. 8
380	0.5 hrs.	Holden; No. 6
370	0.1 hrs., <i>ca.</i>	Koenigsberger
370	0.3 hrs.	Simon; in H
330	0.3 hrs.	Simon; in O
310	2 hrs.	Simon; in O
310	4 hrs.	Simon; in H
310	2-3 hrs.	Holden; No. 8
310	3-4 hrs.	Holden; No. 6
300	4 hrs.	Simon; in O
295	6-7 hrs.	Koenigsberger
290	48 hrs.	Simon; in H
275	5 hrs.	Holden; No. 8
275	20-30 hrs.	Holden; No. 6
235	30-35 hrs.	Holden; No. 8
235	80 hrs., <i>ca.</i>	Holden; No. 6

If a curve is plotted from these concordant data, time being the abscissae, temperature the ordinates, it will be of the parabolic type. The curve is very steep between 300 and 400°, finally merging into the vertical axis, where time = 0. At lower temperatures the curve rapidly flattens out until it is practically horizontal at 225°, which may be taken as the minimum decolorization temperature of smoky quartz, and the maximum temperature at which smoky quartz can have existed in nature (see section III). Tests on sixteen specimens of smoky quartz, from all four of the color classes, showed that in every case the color disappeared after heating for shorter or longer periods at $240 \pm 10^\circ$. The results are given in Table VIII. It is evident that there is a general tendency for the darker specimens to require a longer time for decolorization than the lighter ones.

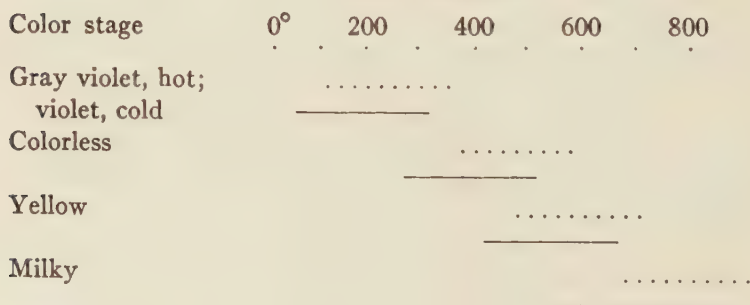
TABLE VIII. TIME NECESSARY FOR DECOLORIZATION OF SMOKY QUARTZ AT $240 \pm 10^\circ$

Specimen number	1	2	4	12	24	25	26	27	31	3	9	11	21	28	29	10
Color-class	i	i	i	i	i	i	i	i	i	ii	ii	ii	ii	iii	iii	iv
Time (days)	5	2	4	2	9	9	9	2	7	2	2	2	2	2	5	1

When hot, smoky quartz has a pronounced yellowish-greenish to blackish-greenish color. If the heating is not prolonged until decolorization ensues, the original color is regained on cooling. The decolorization of smoky quartz by heat can be explained as being due to the oxidation of silicon atoms, causing them to revert to their original character as parts of the quartz lattice.

The decolorization of amethyst takes place at a higher temperature than that of smoky quartz. After eighty-two hours at 235°, only one of the three specimens tested showed any appreciable change of color, and it lost only a portion of its original color. After forty-nine hours at 305-315° the other two specimens were partially decolorized, but several hours heating at 385-420° were necessary to completely remove the color. This agrees with the results of other investigators. For most specimens of amethyst the minimum temperature at which the color is unstable may be given as $260 \pm ^\circ$. At lower temperatures, amethyst is always a gray violet when hot, though it again takes on its original color when cooled to room temperature. Further heating after the colorless stage has been reached often produces a citrine yellow color, especially in the darker specimens, as is well known. This is supplanted by an opaque milkiness at still higher temperatures. The diagram below shows the approximate temperature ranges of the various color stages.

FIGURE 3. TEMPERATURE RANGES OF THE SEVERAL COLOR STAGES OF AMETHYST, WITH SHORT HEATING; ———, WITH LONG HEATING.



The change from violet to yellow, on heating, may be interpreted as due to the disintegration of a violet ferric compound to a simpler, yellow, ferric compound, possibly the oxide. This is further discussed in part VI.

The changes in absorption spectra caused by heating smoky quartz and amethyst are described in the next section.

VI. THE TRANSMISSION OF LIGHT BY SMOKY QUARTZ AND AMETHYST

Frequently the manner in which a mineral transmits light will give a clue to the chemical nature of the pigment. For this reason the transmission of light through several specimens of smoky quartz and amethyst was measured. Heat-decolorized specimens were also studied in the same way, as well as a section of rock crystal which had been colored by radium radiation.

REVIEW OF THE LITERATURE

Nabl (20) compared the spectra of amethyst, "burnt amethyst," which had been changed to yellow by heat treatment, and citrine. The amethyst possessed an absorption maximum in the green. After its color had been changed to yellow by heat, the absorption spectrum was identical with that of natural citrine. Nabl concluded that the spectrum of amethyst is identical with that of ferric sulfocyanate, and advanced the hypothesis that the violet color is due to that compound. However, neither the character of the absorption nor the color of ferric sulfocyanate solutions agree with those of amethyst. The maximum of absorption of ferric sulfocyanate in amyl alcohol is at $0.516\mu^{18}$, while in amethyst it is at $0.53\text{--}0.54\mu$. The color of sulfocyanate solutions is an almost pure red (Ridgway 72) while that of amethyst is violet (63'). Added to these objections is the consideration that compounds of this nature have not been found to exist among minerals.

Vanzetti (55) found that the maximum of absorption of light by smoky quartz is in the violet portion of the spectrum.

NEW OBSERVATIONS

The measurements here reported were made in the Physics Laboratory of the University of Michigan. The instrument used was a photospectrometer with a variable sector disk. Polished sections, or crystals with smooth faces, were employed in this work. The results are graphically shown in Figures 4 and 5. The abscissae represent the wave lengths of the transmitted light in μ , the ordinates, the percentage of the incident light which was transmitted through the sections.

¹⁸ J. Formanek: DIE QUALITATIVE SPEKTRALANALYSE.

In Figure 4, Diagram 1, are given several transmission curves for a single section of smoky quartz. Curve *1a* gives the transmission of ordinary light passing through the section in a direction parallel to the vertical axis. There is a gradual and steady increase in the percentage of incident light transmitted as the wave length increases. The curves marked ω and ϵ were obtained by passing plane polarized light through the section in a direction perpendicular to the *c* axis. These curves give the transmission for the ordinary and extraordinary rays, respectively. The somewhat yellowish cast of the color for ϵ is due to the convexity of the

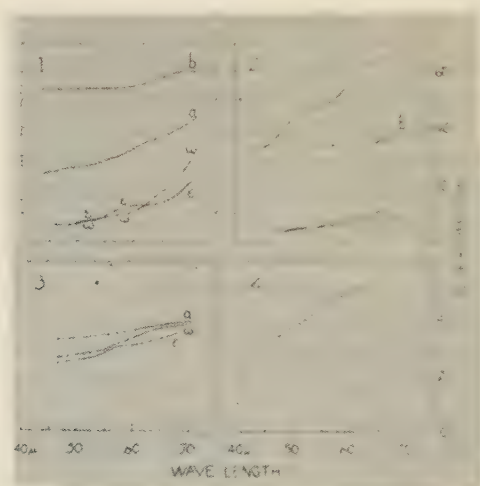


FIG. 4

curve near 0.60μ . The curves also demonstrate that the absorption is $\epsilon > \omega$, as stated previously (part II). In these and later curves, too much attention must not be paid to the absolute amount of transmitted light. The more important feature is the shape of the curve, for the percentage of transmitted light varies with the thickness and clearness of the section.

The section, the transmissibility of which is given in curve *1a*, was heated at $235 \pm 10^\circ$ for twenty-two hours, which caused decolorization. New measurements, plotted in curve *1b*, were then made. The direction of the passage of light is the same as in curve *1a*, so that the two curves are comparable. As would be expected, the heat treatment markedly increased the transmission of light,

and the transmission is about the same for all parts of the spectrum except that it is somewhat greater in the red. This is because decolorization was not quite complete.

In Figure 4, Diagram 2, are given curves for three more specimens of smoky quartz. Curve *2a* is similar to *1a*. The specimen represented by *2b* was very pale, and therefore its transmissibility is like that of heat-decolorized smoky quartz, *1b*. Curve *2c* shows the transmission of ω and ϵ in another section.

The transmissibility of rock crystal which has been colored smoky brown by radiation (diagram 3) is exactly like that of natural smoky quartz, as a comparison of diagrams 3 and 1 shows. Even the convexity in the curve for ϵ , near 0.60μ , is found in the radiated quartz.

Since it has been suggested¹⁹ that smoky quartz may owe its color to dispersoid silicon, the transmissibility of a solution of colloidal silicon was measured. This solution was prepared by producing an electric arc between two bits of silicon held under isobutyl alcohol. The curve for the colloidal silicon solution (curve 4) is very similar to that for smoky quartz, apparently making it possible that the pigment actually is colloidal or dispersoid silicon. Not too much stress should be laid on this, however, for it must be pointed out that many other elements give the same brown color when in colloidal solutions prepared by the electric-arc-dispersion method.

In Figure 5, curves *1a* and *1b*, *2a*, and *3a*, show the transmission of light through amethyst. The curves are alike and show that amethyst has a maximum of absorption near $0.53\text{--}0.54\mu$ in the yellow-green. This color, being complementary to violet, is responsible for the hue of amethyst.

Curves *3a* and *3b* show the effect of heat treatment on amethyst. Curve *a* is for the original violet section. After being heated for one-half hour at 400° it became yellow, giving the transmission plotted in *b*. The latter curve is similar to those of citrine, *4a* and *4b*. These observations agree with those of Nabl (20), therefore, in showing that "burnt amethyst" and citrine have the same pigment, which is probably some simple compound of ferric iron. The transmissibility of a colloidal hydrous ferric oxide solution was measured (curve *4c*) and found to be entirely similar to that of citrine.

¹⁹ Koenigsberger and M  ller: *Centr. Mineral.*, 1906, 73, foot-note.

The violet pigment of amethyst is, then, probably a ferric compound, which is decomposed by heat to the yellow citrine pigment. The fact that the paler amethyst specimens do not give the yellow color on heating is probably due to a greater pigmenting power of the violet compound than the yellow one. The intermediate colorless stage may be due to a chromatic neutralization of the nearly complementary yellow and violet colorations.

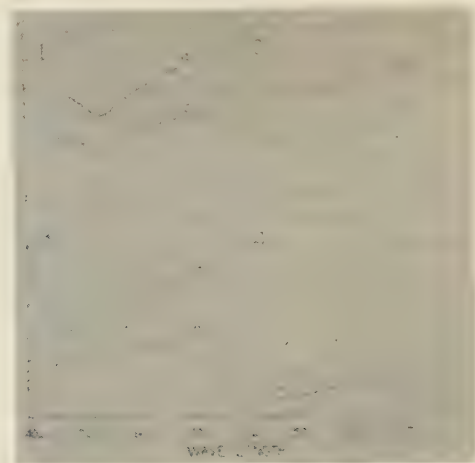


FIG. 5

While most ferric compounds are yellow or red in color, they frequently show a distinct, though slight, absorption maximum near 0.52μ ²⁰ This is the region in which FeSCN absorbs strongly. In view of the well known variations in the position and intensity of absorption by an ion depending upon its chemical environment, it may be said that the fact that amethyst has an absorption maximum at 0.53μ is in agreement with the hypothesis that it has a ferric pigment.

Some ferric compounds have the same color as amethyst. It has been definitely proven that the violet ferric ammonium alum owes its color not to any impurity, but to the iron itself.²¹ If the alum is crystallized from an excess of sulfuric acid to prevent the

²⁰ Well shown for FeCl_3 in plate 51A of H. C. Jones and J. A. Anderson's *Absorption Spectra of Solutions: Carnegie Inst. Publ.*, **110**, 1909.

²¹ Jane Bonnell and Edgar Perman: *J. Chem. Soc.*, **119**, 1994 (1921).

formation of hydrous ferric oxide by hydrolysis, the crystals are violet. Their color exactly matches the hue of amethyst.

Curves 2*a* and 2*b* of Figure 5 are of interest in showing the transmissibility of a violet area (curve *a*) and a smoky brown area (*b*) in the same zonally colored crystal. The curves are like those of uniformly colored crystals of the same hues, respectively.

VII. THE IMPURITIES IN SMOKY QUARTZ

Besides the theory that smoky quartz has been colored by the action of radium radiations, it has been suggested that its color may be due to trivalent titanium or to hydrocarbon compounds. The results of analytical work on the mineral will be given in this section, with a discussion of their application to all the theories that have been proposed to account for the color.

ANALYSES OF SMOKY QUARTZ

A detailed analysis was made on a twenty-five-gram sample of the dark colored smoky quartz No. 1, in order to discover what possible pigmenting elements might be present. The finely ground quartz was decomposed by means of hydrofluoric and sulfuric acids. The results of the analysis appear in Table IX, with a similar analysis for amethyst No. 1.

The elements which might cause a coloration, and which were found by this analysis, are iron, titanium, and manganese. Therefore these impurities were determined on seventeen specimens of all depths of color (Table X). The method of analysis was as follows: Samples of finely ground quartz, of five to six grams weight, were decomposed in platinum dishes by means of HF and H₂SO₄. The sulfuric acid solution finally obtained, diluted with water, was first analyzed for TiO₂ by the peroxide colorimetric method. The yellow coloration was then discharged by reduction with SO₂ water, and the excess of SO₂ was boiled off. Manganese was next determined colorimetrically by the KIO₄ method. The periodate was then reduced with SO₂, and the liberated iodine was boiled off. The solution was evaporated until fumes of SO₃ appeared and, after dilution, Fe₂O₃ was determined by titration with N/200 KMnO₄.

TABLE IX. DETAILED ANALYSIS OF SMOKY QUARTZ NO. 1 AND AMETHYST NO. 1

	Smoky quartz	Amethyst	Remarks
Loss on ignition (H_2O, CO_2)	0.06%	0.09%	
Al_2O_3	.06	.06	By difference from the combined Al and Fe precipitate
CaO	.04	.03	Ammonium oxalate precipitation
Fe_2O_3	.003	.05	$KMnO_4$ titration
UO_3	.00x	none	Sodium phosphate bead test
TiO_2	.001	.001	H_2O_2 colorimetric method
Rare earth oxides	.001	trace ?	KOH precipitation
MnO	.0001	.0001	KIO_4 colorimetric method
CoO	.0000+	present, < .0001	Borax bead test
MgO	trace	trace	Ammonium phosphate precipitation
Na_2O	trace	present	Spectroscopic tests
Li_2O	trace	present	
K_2O	trace?	trace?	
ZrO	trace?	trace?	Tumeric paper test
Cr_2O_3	none	trace?	Borax bead test
SrO, BaO	none	none	Spectroscopic tests on the calcium precipitate
Au	none	none	Phenylhydrazine acetate test
W	none	none	Stannous chloride test
Sn	none	none	Ammonium molybdate test

In the analyses great care was taken to avoid introducing impurities through the reagents, all of which were analyzed for iron, titanium, and manganese. Only iron was found in any of them, and that only in small amounts. Proper corrections, never exceeding 0.4 mg. Fe_2O_3 , were made on the final determinations.

HYPOTHESES CONCERNING THE PIGMENT

The several theories which have been advanced in explanation of the cause of color in smoky quartz have been outlined in the introduction. In section IV evidence was given favoring a coloration through the action of radioactive substances. It is now

TABLE X. ANALYSES OF SMOKY QUARTZ FOR Fe_2O_3 , TiO_2 , AND MnO

Color-class	Specimen number	Fe_2O_3	TiO_2	MnO
i	1	0.003%	0.001%	0.0001%
	2	none ¹	.001	none ³
	4	none	.001	none
	6	.03	.002	.0005
	24	.001	.002	.0003
	25	.001+	.001+	.0005
	31	none	.001	.0004
ii	3	.001	.001	none
	5	.008	.008	none
	7	.001	trace ²	.0002
	9	.003+	.001	.0001
	21	.004	trace	.0002
iii	18	.003+	.001	none
	28	.005	trace	.0002
	29	none	trace	.0001
	30	lost	.001	.0001
iv	10	.003	trace	none

¹ "none" = less than 0.001% Fe_2O_3 , the smallest amount detectable

² "trace" = less than 0.001% TiO_2

³ "none" = less than 0.0001% MnO

necessary, first, to examine the evidence for and against the other theories, and second, to present experimental results further substantiating the radiation hypothesis.

CARBON COMPOUNDS—A number of investigators have concluded that smoky quartz owes its color to the presence of hydrocarbon pigments. Forster (7) and Wright (9) obtained extremely small amounts of oily liquids by heating large samples of smoky quartz fragments. This led them to think that the color was due to hydrocarbons. Berthelot (28) thought the pigment was a carbon compound because smoky quartz is decolorized by heating, with an "organic smell."

Kraatz-Koschlau and Wöhler (18, 91) also advanced the hypothesis that smoky quartz was colored by a hydrocarbon, on the basis of such criteria as (a) decolorization simultaneously with

the production of a "burnt smell"; (b) pyrophosphorescence; (c) the browning of the powder on being heated with concentrated H_2SO_4 ; (d) the determination of CO_2 and H_2O on igniting the ground mineral in an oxygen current. Several investigators have found very pertinent reasons for disbelieving that these features indicate the presence of a hydrocarbon pigment.

Weinschenk (15) has observed that colorless quartz occurs in sedimentary rocks full of carbonaceous substances, while colored quartz is found in pegmatites, where hydrocarbon pigments could not have existed. Later (23) he replied to Kraatz-Koschlau and Wöhler, saying that the "odor of organic matter," "browning of the powder," and pyrophosphorescence are as easily produced on powdered glass as with a colored mineral.

It is entirely unnecessary to heat quartz powder in an oxygen stream to obtain CO_2 and H_2O as they are practically always present in the original specimens as liquid and gaseous inclusions. It is not permissible to recalculate the CO_2 and H_2O found in this way, to C and H, and to assume the presence of hydrocarbons on that evidence.

In this investigation a large sample of dark smoky quartz was analyzed to determine whether it would yield any colored hydrocarbon liquid. A forty-two-gram sample of specimen No. 4 was ground after careful washing with concentrated nitric acid, water, alcohol, and ether. The powder was soaked successively in alcohol, ether, and chloroform, for from seven to nineteen hours in each case. The decant liquids were evaporated to a smaller volume than that of the quartz sample, but they remained colorless.

The powder was then heated to decolorization in a retort, but only a colorless liquid, neutral to litmus, was obtained. This was undoubtedly water. The results, then, were entirely negative. The previous determinations, by other investigators, of oily brown liquids obtained by distillation from smoky quartz may probably be ascribed either to imperfect cleaning of the specimens, or to the presence of inclusions in the quartz. Quartz has been known to contain cavities filled with petroleum or asphalt.²²

TITANIUM—Weinschenk (15,16) ascribed the color of smoky quartz to Ti_2O_3 in dilute solid solution, because he had obtained a

²² Cf. H. Davy: *Phil. Trans. Roy. Soc.*, **1822**, 367-374; C. L. Reese, *J. Am. Chem. Soc.*, **20**, 795-797 (1898); Dana's *System Mineralogy*, 4th edition, **II**, 150 (1854).

positive test for titanium in several specimens in which he detected no rutile.

The analyses given in Table X shows that the small amount of titanium found in smoky quartz is quite uniform from the darker to the paler specimens. If the color were due to that element, the darker specimens should contain decidedly more than those which were pale. Furthermore, amethyst contains approximately as much titanium as smoky quartz (Table XIII) and rose quartz considerably more.²³ An examination of the specimens of smoky quartz showed in many cases minute needle-like inclusions, which are believed to be rutile, accounting for the presence of titanium in smoky quartz. It is therefore concluded that this variety of quartz does not owe its color to titanium.

IRON AND MANGANESE—As in the case of titanium, the low percentages of iron and manganese occurring in smoky quartz have no apparent relation to the color. They have never been suggested as possible pigments for this mineral, as far as could be ascertained.

URANIUM—It has been shown that none of the pigmenting elements found in smoky quartz can account for its color. Earlier in this paper the theory that smoky quartz has been colored by the action of radiations has been supported and elaborated. It is therefore of considerable interest to determine whether smoky quartz contains appreciable amounts of radioactive elements.

Large composite samples (twenty-four to thirty-four grams) were employed in determining uranium. There were two samples for color class i, the darkest specimens. One was of specimens from radioactive pegmatites of Ontario. The other was a composite of specimens which did not occur in notably radioactive rock bodies, as far as known. The separation of uranium was carried out by Scholl's method.²⁴ When all interfering elements had been removed, a little AlCl_3 solution was added to aid in carrying down the uranium hydroxide. Sodium phosphate beads of the ignited precipitate were compared with standard uranium beads. The results are given in Table XI.

²³ Edw. F. Holden: *Am. Min.* **9**, 75-88, 101-108 (1924).

²⁴ U. S. Bureau of Mines Bull. **212**, 230 (1923).

TABLE XI. ESTIMATED PERCENTAGES OF UO_3 IN SMOKY QUARTZ

Sample	Color-class	Composite of smoky quartz specimens	% UO_3	Grams UO_3 per 100 grams of quartz
I	i	1, 2, 4, 6, 12, 31	0.006%	6×10^{-3}
II	i	23, 24, 25, (from radioactive pegmatites of Ontario)	.002	2×10^{-3}
III	ii	3, 5, 7, 9, 21	.001	1×10^{-3}
IV	iii and iv	10, 18, 28, 29, 30	.001	1×10^{-3}

The ignited precipitate of sample I was a decided green. The amount of UO_3 indicated by these analyses is about fifty times greater than that ordinarily found in colorless quartz. Strutt²⁵ has determined, in four specimens of quartz, an amount equal to 2 to 13×10^{-5} grams UO_3 per 100 grams quartz. It was not possible to detect any uranium in amethyst (Table XIII) or rose quartz.²⁶ In view of the small amount of disintegration necessary to produce a color when a mineral is radiated, the percentages of UO_3 in smoky quartz are significant. This is especially so since the determinations probably give only a minimum percentage, due to the difficulty of completely separating traces of elements. The amount of UO_3 is greater in the darker specimens, and less in the lighter. It is of interest to note that sample I contained more uranium than sample II, of the same color class, though the latter is from strongly radioactive rocks. In the Ontario occurrence the near presence of active material outside the quartz could easily have colored it.

In order to determine radium, a large, composite sample of 102 grams from specimens Nos. 1, 4, 18, and 31 was prepared. The entire residue, after the silica was driven off with HF and H_2SO_4 , was washed into a flask, which was sealed so that the radium emanation might accumulate. The sample showed decided activity when tested in an emanation electroscope. Approximately 4×10^{-10} grams Ra per 100 grams of quartz were found to be present. This is equivalent to 0.001% UO_3 , which is of the order of the amount found by direct analysis. The two methods therefore check in showing that smoky quartz contains many times more radium and uranium than is ordinarily found in quartz. Given the necessarily great time element, such amounts of radium could

²⁵ R. J. Strutt: *Proc. Roy. Soc.*, **80A**, 588 (1908).

²⁶ Edw. F. Holden: *Am. Min.* **9**, 75-88, 101-108 (1924).

well cause the color of smoky quartz. The possible presence of thorium, which was not tested for, would increase the strength of the radiations.

FREE SILICON—Having found support for the radiation theory of coloration in the presence of radium and uranium, it became necessary to test the further assumption that the coloration was due to the liberation of free silicon by the radiations. It is very difficult to determine the presence of traces of elemental silicon, but a method was devised which gives results that may, perhaps, be regarded as fairly good evidence of the presence or absence of free silicon.

The principle of the method is that amorphous silicon is attacked and oxidized by aqua regia. If this occurs, it would be expected that the newly produced silica would form as the colloidal hydroxide, which might be filtered off and recovered by the evaporation of the filtrate. Certain precautions as to blanks must be taken.

The quartz was finely ground and was treated for a known period with boiling aqua regia of definite concentration. The acid was quickly diluted with water and was filtered through two quantitative filter papers. After the addition of sulfuric acid, the filtrate was evaporated until SO_3 fumes appeared. The beaker was then carefully washed out into a weighed platinum dish. Evaporation to dryness was followed by ignition. After the residue was weighed, the silica was volatilized with HF , and the residue again weighed. The difference between these weighings gave the amount of silica recovered by this process.

Blanks were run with definite weights of rock crystal powder, using the same amount and concentration of acid as in the smoky quartz tests. The time was also the same. This determined what amount of the finely ground quartz would be carried into colloidal solution when treated with hot aqua regia. All of the silica recovered from the smoky quartz in excess of the blanks was assumed to be derived from free silicon. In this way a minimum determination of the amount of free silicon in the quartz was obtained. The proportion of the total amount present that is recovered, of course, depends largely upon the fineness of grinding. In order to keep this factor as uniform as possible, large samples were ground, and each sample was divided into two parts. One was decolorized by gentle heating while the other was untreated. The amount of silica recovered from both the original and the heat-decolorized

specimens was thus determined. In the same way, a sample of rose quartz which had been radiated until it became smoky brown was divided and one half was decolorized. A sample of unirradiated rose quartz was analyzed in the same manner as those which had been radiated. The results of these analyses are given in Table XII.

TABLE XII. AMOUNT OF SILICA RECOVERED FROM SMOKY QUARTZ, ROCK CRYSTAL, AND RADIATED ROSE QUARTZ

	Sample	Grams SiO ₂ recovered per gram of quartz	
		Original sample	Heat-decolorized sample
Blanks	Rock crystal	$2\frac{1}{2} \times 10^{-5}$	_____
	Rock crystal	$3\frac{1}{2}$	_____
	Rock crystal	$4\frac{1}{2}$	_____
Color-class i	Smoky quartz No. 1	11 ¹	_____
	Smoky quartz No. 4	10	6×10^{-5}
	Smoky quartz No. 31	8	5
Class ii	Smoky quartz No. 3	8	5
Class iii	Smoky quartz No. 18	7	3
	Rose quartz	6	_____
	Radiated rose quartz	11	4

¹ Average of three determinations.

The decolorized smoky quartz and decolorized radiated rose quartz gave about the same amount of silica as the rock crystal blanks. This is interpreted to be colloidal silica taken up by the action of the acid, rather than oxidized free silicon, but the original smoky quartz and radiated rose quartz specimens show significant excesses of recovered silica over the blanks and heated specimens. This appears to be an indication that they contain free silicon in appreciable amounts. It is to be noted that the darker specimens of smoky quartz contain more free silicon than the paler, which is to be expected if silicon is the coloring agent. The figures given in Table XII represent the minimum amount of recoverable silica derived from free silicon. It would probably be quite safe to place the actual percentage of silicon in the darker smoky quartz specimens as of the order of 0.01 per cent.

There are possible objections to the conclusion that these experiments indicate the presence of free silicon in smoky quartz and radiated quartz. It might be argued that the silica recovered by the process is obtained from an included hydrated alkaline silicate of a nature similar to that of the zeolites. Heating that type of compound would cause partial dehydration, and then it would less readily yield silica; but such an assumption does not explain why radiated rose quartz gives up considerably more silica than the unradiated type, and still more than the rock crystal. We are forced to conclude that there is a fairly strong indication of the presence of free silicon in smoky quartz, even though the evidence cannot be positive, due to analytical difficulties.

SUMMARY

It is probable that smoky quartz contains free silicon, which was liberated by radiation, and is responsible for the color of that mineral. This cannot be certainly and unquestionable proven, but the evidence given above indicates such to be the case. The presence of significant amounts of uranium and radium is also very important, for it adds to the evidence for coloration by radiation. No evidence for the presence of hydrocarbon pigments or of coloration by trivalent titanium was obtained.

VIII. THE IMPURITIES PRESENT IN AMETHYST

The results of the analyses of amethyst are given in this section, together with a discussion of the hypotheses that amethyst is colored by (a) hydrocarbons, (b) by a compound of manganese, and (c) by an iron compound.

ANALYSES OF AMETHYST

In order to determine what impurities were found in amethyst, a detailed analysis was made on nineteen grams of specimen No. 1, which was very dark colored. The results have been given in Table X, in part VII.

The elements which might possibly enter into the pigment are iron, manganese, and titanium. Analyses for these impurities were therefore made on seventeen specimens, as shown in Table XIII. The methods of analysis were similar to those employed for smoky quartz, except that iron was determined both by titration and

colorimetrically, by the improved HSCN method.²⁷ The results of the Fe_2O_3 analyses by the two methods agreed very well, though for the amounts of iron encountered the titration method was the more accurate.

TABLE XIII. ANALYSES OF AMETHYST FOR Fe_2O_3 , TiO_2 , AND MnO

Color-class	Specimen number	Fe_2O_3	TiO_2	MnO	Average % Fe_2O_3
i	4	0.35%	trace ¹	0.0002%	0.14%
	14	.24	0.0005%	.0001	
	3	.06	trace	none ²	
	1	.05	.001	.0001	
	7	.02	trace	none	
ii	19	.07	.001	.0080	.026
	13	.03	.001	.0011	
	17a ³	.02	trace	.0015	
	18	.006	trace	.0002	
	23	.005	trace	.0002	
iii	12	.011	trace	.0004	.007
	15	.007	trace	.0002	
	11	.006	trace	none	
	8	.005	trace	.0001	
iv	9	.015	trace	.0002	.007
	17b ³	.004	.001	.0021	
	2	.004	trace	.0002	

¹ "trace" = less than 0.001% TiO_2

² "none" = less than 0.0001% MnO , the smallest amount detectable

³ 17a and 17b are dark pale portions of the same specimen

In part I the various theories proposed to account for the color of amethyst have been outlined. The hypothesis of coloration by radium radiation is discussed in part IV, where it has been found to be inapplicable.

CARBON COMPOUNDS—Kraatz-Koschlau and Wöhler (18, 19) have suggested that amethyst, as well as smoky quartz, is colored by a hydrocarbon, though possibly manganese has some connection with the amethyst pigment. Specimens from Brazil and Schemnitz obeyed all the criteria which they had given as indicat-

²⁷ H. N. Stokes and J. R. Cain: *Sci. Papers, U. S. Bureau of Standards*, Nos. 53 and 54 (1907).

ing a hydrocarbon pigment (see part VII). Simon (36) detected traces of CO_2 and H_2O in amethyst, but he found more in colorless rock crystal. Other writers, in supporting their own theories, have disputed the possibility of a hydrocarbon pigment in amethyst [Doelter (42) and Heintz (6)].

MANGANESE—The theory that manganese compounds color amethyst was proposed by Berthelot (28). He treated quartz by radium radiation and decided that the violet color was due to a trivalent manganese compound, largely from analogy with the behavior of glasses containing a trace of manganese. There are several valid objections to this hypothesis. In the first place, the cause of the violet coloration of glass by radium is not definitely known, and it is the subject of dispute among authorities²⁸ It is not generally accepted that the color is due to manganese. Small amounts of manganese impart a pink, not a violet, color to glasses. Furthermore, rose quartz, the color of which is probably due to manganese,²⁹ is pink, and its color is not deepened by radium radiations as is that of amethyst. Instead, both the original and heat-decolorized specimens of rose quartz always become smoky brown when radiated.

Watson and Beard (43), too, believed that amethyst has a manganese pigment. This conclusion was based on four analyses which are in general agreement with those of Table XIII. It is to be noted that they regarded the coloration of rose quartz as due to an organic compound, although their analyses showed that it had on the average about as much manganese as amethyst. The high content of iron in amethyst was disregarded.

The analyses in Table XIII show that the amount of manganese in amethyst does not vary with the depth of color. With the exception of specimens Nos. 19, 13, 17a, and 17b, the amount of MnO is very small. Specimens Nos. 19, 17a, and 17b differ from the others analyzed in being massive specimens from ore veins, which accounts for the relatively high MnO content. The amount of manganese in No. 17b, a pale portion of the same specimen from which No. 17a was taken, is more than in No. 17a, the darker colored part. Specimen No. 13 contains canals filled with black manganese dioxide, easily visible to the eye. It is concluded, therefore, that manganese does not color amethyst.

²⁸ Cf. S. C. Lind: *J. Phys. Chem.*, **24**, 437-443 (1920).

²⁹ Edw. F. Holden: *Am. Min.* **9**, 75-88, 101-108 (1924).

TITANIUM—The amount of titanium is small and rather uniform from the dark to the pale specimens. It is probably due to the small rutile inclusions often seen in quartz.

IRON—The suggestion that an iron compound is the pigment of amethyst has been the one most often made. Poggendorff (2) suggested that it might be colored by an iron acid. Heintz (6) analyzed a specimen from Brazil and found 0.020 per cent Fe_2O_3 and less than 0.01 per cent MnO . He, also, believed that an iron acid might be the pigment. The change of color on heating would be due to the formation of a yellow oxide. Engler and Knies (11) proposed a ferric carbonate as the pigment. Hermann (34) thought the color might be due to the presence of ferrous, ferric, and manganese compounds. The action of heat, producing a yellow color, might be due to the loss of the violet manganese color, allowing the yellow iron color to predominate.

Nabl (20) has advanced the belief that FeSCN is the pigment of amethyst. Objections to his conclusions, drawn from the absorption spectrum, are given in part VI. His analytical results will now be discussed. Nabl found sulfur in a fusion of amethyst powder with soda and niter. Kraatz-Koschlau and Wöhler (19) tried to verify this determination, and ignited the quartz powder in a stream of oxygen which was led through sodium hypobromite. The solution was tested for sulfur with negative results. Nabl (22) then repeated his analyses, using new fusion methods, and again obtained positive tests. The apparent discrepancy between Nabl and Kraatz-Koschlau and Wöhler's results is easily accounted for. The presence of sulfates in liquid inclusions in quartz has been noted several times.³⁰ Nabl's methods, involving fusion, recovered the sulfur from the sulfates, but the other investigators, who simply ignited the quartz powder, could not break down the sulfates, though a sulfocyanate would readily have yielded its sulfur. Their results simply show that no FeSCN was present.

Wild and Liesgang (56), using the spectroscopic method, found traces of iron in amethyst. They ascribed the color to that element.

The analyses in Table XIII show that amethyst contains large amounts of iron, and that the percentage of Fe_2O_3 decreases quite

³⁰ E. G. Sorby: *Quart. J. Geol. Soc.*, **14**, 473, 475 (1858); Koenigsberger and Müller: *Centr. Mineral.*, **76**, (1906).

regularly as the specimens become paler in color. The average percentage of Fe_2O_3 for each of the four color-classes is: i, 0.14; ii, 0.026; iii, 0.007; iv, 0.007. This seems clearly to show that some compound of iron is the pigment of amethyst. That view is supported by other evidence already given.

All of the specimens were examined microscopically. Besides the generally present water and carbon dioxide inclusions, needles of goethite and particles of hematite were frequently found. These inclusions of iron compounds are most abundant in the darker colored specimens, and are not present at all in the paler ones. In Table XIII analyses Nos. 1, 3, 4, 14, and 19 are those in which part of the iron was contributed by these visible inclusions, which it was not possible to eliminate. The other specimens chosen for analysis are free of such particles.

Endeavoring to separate the visible hematite inclusions from the iron compounds of submicroscopic dimensions, which must form the pigment, the powder of specimens Nos. 3 and 4 was leached with HCl , before the usual treatment with HF . In both cases the iron was practically all dissolved by the HCl , as shown in Table XIV. An absolutely clear fragment of No. 7, which showed no inclusions under the microscope, was then analyzed in the same way. Again, all the iron was taken up by the HCl , showing that the visible hematite or goethite cannot be separated from the remainder of the iron compounds in this manner, for the ferri-ferous pigment is as completely soluble in HCl as is hematite. But, the very fact that iron oxide inclusions are most abundant in the darker specimens of amethyst, and are entirely absent in those which are pale, is evidence in favor of an iron compound as the pigment. Even if analyses Nos. 1, 3, 4, 14, and 19 were omitted, the variation of iron content with depth of color is still very evident.

TABLE XIV. SOLUBILITY OF THE IRON COMPOUNDS IN AMETHYST

Specimen	Per cent Fe_2O_3 leached out by HCl	Remainder of Fe_2O_3	Total per cent of Fe_2O_3
3	0.05 per cent	0.008 per cent	0.06 per cent
4	.34	.007	.35
7	.018	none	.018

IX. SUMMARY AND CONCLUSIONS

SMOKY QUARTZ

Smoky quartz occurs most typically in the drusy cavities of pegmatites and the similar Alpine type of veins. It is formed in the temperature range of about 101° to 220° C., crystallizing from solutions containing carbon dioxide and other mineralizers.

The heat-decolorization of smoky quartz is a time-temperature reaction. Decolorization is complete and immediate at 400° , but continued heating at 235° will cause practically complete loss of color. When hot, the mineral is yellowish- to blackish-green, but if heating was not too prolonged, it regains its original color on cooling.

The light transmitted through smoky quartz is strongest in the red and steadily decreases to the violet end of the spectrum. The absorption is $e > o$ with e slightly more yellowish than o .

The amount of iron, titanium, and manganese in the mineral is small, and bears no relation to the depth of color. The pigment cannot be a hydrocarbon.

It seems probable that smoky quartz owes its color and the property of scattering light to particles of free silicon, of atomic, not colloidal, dimensions. It is believed that small amounts of that element are liberated by the radiations from radioactive substances present in the quartz or in the solutions from which it crystallized. The principal points of evidence in favor of this hypothesis may be summarized as follows:

a) Smoky quartz is characteristically associated with radioactive minerals.

b) Nearly all quartz becomes smoky brown when radiated with radium compounds.

c) The color of heat-decolorized smoky quartz is restored by radiation, and the color of pale specimens may be deepened in that manner.

d) The dichroism and the absorption spectrum of smoky quartz agree exactly with those of radiated rock crystal which has become smoky brown.

e) Smoky quartz strongly scatters light, and this property seems to be correlated with the coloration, for the dark specimens scatter light more strongly than the pale ones, and the scattering disappears with the color when the specimens are heated.

f) The smoky quartz specimens examined in this study contained appreciable amounts of uranium, with radium in equilibrium.

g) Experiments have indicated the probable presence, in smoky quartz, of free silicon, which is oxidized by heat, causing decolorization. Both uranium and silicon are most abundant in the darker specimens.

The hypothesis which has been presented and supported above seems to fit the experimental evidence quite well. Originality for the idea here presented is not, of course, claimed, but additional evidence has been submitted and the theory modified so as better to satisfy the experimental results.

AMETHYST

Amethyst is characteristically zonally colored. It is generally found in amygdaloidal cavities of basic igneous rocks, or cavities in pegmatites. It crystallizes from hot aqueous solutions. It forms at 90° to 250° C., under lower pressure and higher temperature than is normal at the depth where crystallization takes place.

The color of pale amethyst is deepened by radium radiation, and decolorized specimens become violet again. However, naturally colorless quartz rarely becomes violet when radiated, but usually takes on a smoky brown coloration. Amethyst does not noticeably scatter transmitted light. The violet color is unstable at 260°, when amethyst becomes colorless. When hot, below 260°, it is gray violet, but resumes its original color on cooling.

Manganese and titanium cannot be the coloring agents, since they are present only in small amounts which do not vary with the depth of color.

It is concluded that amethyst is colored by a compound of ferric iron, stable up to 260°, and causing absorption of light at 0.53-.54 μ . Other hypotheses of the cause of color in this mineral are not in accord with the experimental evidence. The chief points favoring a ferric pigment, briefly stated, are:

a) Iron minerals are characteristically associated with amethyst.

b) The absorption maximum of amethyst is very near that of some ferric compounds.

c) Certain ferric compounds have the same color as amethyst.

d) Upon being heated, darker amethysts become identical in color and absorption spectrum with citrine, which is thought to be colored by a ferric compound.

e) The amount of iron in amethyst is large, and it varies in porportion to the depth of color.

X. CHRONOLOGICAL BIBLIOGRAPHY OF IMPORTANT PAPERS ON SMOKY QUARTZ AND AMETHYST

1821. 1. BREWSTER, DAVID. On circular polarization, as exhibited in the optical structure of amethyst, with remarks on the distribution of coloring matter in that mineral. *Trans. Roy. Soc. Edinburgh*, **9**, 139-152.
1841. 2. POGGENDORFF, J. C. Formation of iron acids by a galvanic process. *Pogg. Ann. Physik*, **54**, 353-377.
1845. 3. WOLFF, EMIL. The loss on ignition of quartz and fluorite. *J. prakt. Chem.*, **34**, 237.
1854. 4. HAIDINGER, W. The pleochroism and crystal structure of amethyst. *Sitzb. k. Akad. Wiss. Wien., Math.-naturw. Cl.*, **12**, 401-421.
1855. 5. DESCLOIZEAUX, A. Memoir on the crystallization and internal structure of quartz. *Ann. chim. phys.*, **45**, 129-316.
1860. 6. HEINTZ, W. The coloring constituents of flint, carnelian, and amethyst. *Ann. Physik Chem.*, **60**, 519-527.
1871. 7. FORSTER, A. The coloration of smoky quartz. *Pogg. Ann. Physik*, **143**, 173-194.
1881. 8. HAWES, G. W. On liquid carbon dioxide in smoky quartz. *Am. J. Sci.*, **21**, 203-209.
1881. 9. WRIGHT, A. W. The gaseous substances contained in the smoky quartz from Branchville, Connecticut. *Am. J. Sci.*, **21**, 209-216.
1883. 10. BÖKLEM, H. On amethyst. *Neues Jahrb. Mineral. Geol.*, **1**, 62-73.
1887. 11. ENGLER, C., and KNIES, E. Oxygen transfer and the solvent effect of liquid carbon dioxide on metals. *Dingl. prakt. J.*, **263**, 193-200.
1888. 12. JUDD, JOHN W. Development of a lamellar structure in quartz crystals by mechanical means. *Mineralog. Mag.*, **8**, 1-9.
1890. 13. DUFET, H. Comparative measurements on the indices of different quartz specimens. *Bull. soc. franc. mineral.*, **13**, 271-276.
1892. 14. JUDD, JOHN W. Additional notes on the lamellar structure of quartz crystals and the methods by which it is developed. *Mineralog.*, **10**, 123-135.
1896. 15. WEINSCHENK, E. The dilute colorings of minerals. *Z. deutsch. geol. Ges.*, **48**, 704-712.
1896. 16. WEINSCHENK, E. The mineral deposits of the Gross-Venediger stock in the Hohen Tauern. *Z. Kryst.*, **26**, 337-508. (Smoky quartz, 394-403).
- 1896-7. 17. HLAWATSCH, C. The indices of refraction of some pigmented minerals. *Z. Kryst.*, **27**, 605-607.
1899. 18. KRAATZ-KOSCHLAU, K. v., and WÖHLER, L. The natural colorings of minerals. *Tscher. Mineral. Petr. Mitt.*, **18**, 304-333.
1899. 19. KRAATZ-KOSCHLAU, K. v., and WÖHLER, L. The natural colorings of minerals. *Tscher. Mineral. Petr. Mitt.*, **18**, 447-468.

1899. 20. NABL, ARNOLD. The coloring constituents of amethyst, citrine, and burnt amethyst. *Sitzb. k. Akad. Wiss. Wien. Math.-naturw. Cl.*, **108**, 2, Abt. b, 48-57.
1900. 21. KOENIGSBERGER, J. The coloring agent in smoky quartz. *Tscher. Mineral. Petr. Mitt.*, **19**, 148-154.
1900. 22. NABL, ARNOLD. Natural colorings of minerals. *Tscher. Mineral. Petr. Mitt.*, **19**, 273-276.
1900. 22. WEINSCHENK, E. Natural colorings of minerals. *Tscher. Mineral. Petr. Mitt.*, **19**, 144-147.
1901. 24. KOENIGSBERGER, J. Mineral deposits in the biotite-protozone of the Aar massif. *Neues Jahrb. Mineral. Geol., Beil.-Bd.*, **14**, 43-119.
1901. 25. LACROIX, A. (Structure of amethyst). *Mineralogie de la France, etc.*, **3**, 41-45. Paris.
1904. 26. HINTZE, C. (Occurrences of smoky quartz and amethyst). *HANDBUCH DER MINERALOGIE*, **1**, 1346-1441.
1905. 27. EGOROFF, N. Dichroism produced by radium in colorless quartz, and a thermo-electric effect observed on the colored striae. *Compt. Rend.*, **140** 1027-1028.
1906. 28. BERTHELOT, M. Synthesis of amethyst quartz. *Compt. Rend.*, **143** 477-488.
1906. 29. MIETHE, A. The coloring of precious stones by radium. *Ann. Physik*, (4), **19**, 633-638.
1906. 30. WÜLFING, E. A. Mineral pigments. *Festschr. z. 70 Geburtstag, H. Rosensbusch*, 49-67.
1907. 31. BERTHELOT, DANIEL. The coloration of certain precious stones under the influence of radium. *Compt. Rend.*, **145**, 818-820.
1908. 32. DOELTER, C. The effect of radium and Roentgen rays on the colors of precious stones. *Sitzb. k. Akad. Wiss. Wien, Math.-naturw., Cl.* **117**. Abt. 1, 819-844.
1908. 33. DOELTER, C. The effect of radium and ultraviolet light on mineral colors. *Sitzb. k. Akad. Wiss. Wien, Math.-naturw. Cl.*, **117**, Abt. 1, 1275-1325.
1908. 34. HERMANN, WALTER. The effect of oxidizing and reducing gases on the color of some minerals. *Z. anorg. Chem.*, **60**, 369-404.
1903. 35. PHILLIPS, C. E. S. Coloration of glass and quartz by radium. *Nature*, **77** 535.
1908. 36. SIMON, KARL. Mineral colors. *Neues Jahrb. Mineral. Geol., Beil.-Bd.*, **26**, 249-295.
1909. 37. BRAUNS, R. The effect of radium rays on the color of sanidine, zircon, and quartz. *Centr. Mineral. Geol.*, 721-728.
1909. 38. DOELTER, C. The stability of mineral colorations produced by radium. *Centr. Mineral. Geol.*, 232-234.
1910. 39. DOELTER, C., and SIRK, H. The different effects of alpha, beta, and gamma rays on the colors of solids. *Sitzb. k. Akad. Wiss. Wien, Math.-naturw. Cl.*, **119**, Abt. 2a, 1091-1100.
1910. 40. DOELTER, C. DAS RADIUM UND DIE FARBEN. 124-125. *Dresden*.
1913. 41. KOENIGSBERGER, J. A classification of the east Alpine mineral deposits. *Z. Kryst.*, **52**, 151-174.
1915. 42. DOELTER, C. DIE FARBEN DER MINERALIEN, 70-75. *Braunschweig*.

1917. 43. WATSON, T. L., and BEARD, R. E. The color of amethyst, rose, and blue varieties of quartz. *Proc. U. S. Nat. Museum*, **53**, 553-563.
- 1918-19. 44. KOENIGSBERGER, J. Alpine mineral deposits. *Abh. k. Bayer. Akad. Wiss., Math.-phys. Kl.*, **28**, Abh. 10, 11, and 12 (parts I, II, and III).
1918. 45. NEWBERRY, E., and LUPTON, H. Radioactivity and the coloration of minerals. *Mem. Proc. Manchester Lit. Phil. Soc.*, **62**, 1-16, *Nature*, **101**, 198.
1919. 46. STRUTT, R. J. The scattering of light by solid substances. *Proc. Roy. Soc. London*, **95A**, 476-479.
1920. 47. JOHNSEN, A. The paragenesis of alpha quartz and carbon dioxide. *Sitzb. Bayer. Akad. Wiss., Math.-Phys. Kl.*, 321-328.
1921. 48. RAMAN, C. V. Smoky quartz, *Nature*, **108**, 81.
1922. 49. LACROIX, A. (Smoky quartz and amethyst in Madagascar). *MINERALOGIE DE MADAGASCAR*, **1**, 196 et seq. *Paris*.
1922. 50. MEYER, S., and PRZIBRAM, K. Coloring and luminescence produced by Becquerel rays. *Z. phys. Chem.*, **100**, 334-336.
1922. 51. TUTTON, A. E. H. (Structure of amethyst). *CRYSTALLOGRAPHY AND PRACTICAL CRYSTAL MEASUREMENTS*, **1**, 508-510. *London*.
1922. 52. WILD, G. O., and LIESEGANG, R. E. The colorings of some quartz varieties and their instability. *Centr. Mineral. Geol.*, 481-483.
1923. 53. DOELTER, C. Color changes of minerals by radiations. *Centr. Mineral. Geol.*, 321-324.
1923. 54. LIND, S. C., and BARDWELL, D. C. The coloring and thermophosphorescence produced in transparent minerals and gems by radium radiations. *J. Franklin Inst.*, **196**, 375-390; *Am. Min.*, **8**, 171-180.
1923. 55. VANZETTI, B. L. The colloidal nature of some coloring substances in minerals, and the possibility of determining their chemical nature by a spectrophotometric study. *Atti. congresso naz. chim. pura applicata*, 419, (1923).
1923. 56. WILD, G. O., and LIESEGANG, R. E. The color of amethyst and beryl. *Centr. Mineral. Geol.*, 737-740.
1924. 57. TUTTON, A. E. H. (Structure of amethyst). *THE NATURAL HISTORY OF CRYSTALS*, 206-213. *London*.
1924. 58. VANZETTI, B. L. The color of smoky quartz. *Gazz. chim. ital.*, **54**, 95-99.

While this dissertation was going through the press word was received of the tragic death of Dr. Holden who was drowned on August 5th at North Deer Isle, Maine.

CHANGES IN THE CONSTITUTION AND MICRO-
STRUCTURE OF ANDALUSITE, CYANITE, AND
SILLIMANITE AT HIGH TEMPERATURES
AND THEIR SIGNIFICANCE IN IN-
DUSTRIAL PRACTICE*

ALBERT B. PECK, *University of Michigan*

Abstract

Owing to their growing commercial importance in the manufacture of refractories and porcelain, the minerals of the sillimanite group (andalusite, cyanite, and sillimanite) were investigated as to their decomposition products and volume changes between cones 10 and 15.

Petrographic-microscopic examinations showed that andalusite breaks down at cone 13 into mullite and glass, while cyanite also breaks down into the same components but at cone 12. Sillimanite is not decomposed up to cone 15. The composition of the mullite was checked by chemical analysis.

Andalusite shows almost no volume change at dissociation; sillimanite shows a slight expansion up to cone 15; cyanite shows a great expansion and disintegration at dissociation.

The practical significance of the behavior of the minerals is discussed as well as their possibilities for use in ceramic ware. Andalusite could be used in the raw state; cyanite would require calcination before use, so that andalusite appears to be best suited for most bodies.

INTRODUCTION

As a result of heating at high temperatures or of fusion at atmospheric pressure, many aluminium silicate minerals, including andalusite, cyanite, topaz, dumortierite, kaolin, and others, invert or break down into other substances. One product of this change is a crystalline compound which, until very recently, has been interpreted as artificially produced sillimanite with the composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. A knowledge of the conditions under which this alteration takes place is very important because of the use of some of these minerals in industrial processes. This is especially true of the trimorphous group of the minerals andalusite, cyanite, and sillimanite, with which this investigation is concerned.

* From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, June, 1925. This paper was originally printed in essentially its present form in the *Journal of the American Ceramic Society*, Vol. 8, 407-429, (1925), to which permission to reprint is acknowledged.

TRIMORPHISM OF $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$

The compound $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ is trimorphous, forming a group of three minerals, andalusite, cyanite, and sillimanite, generally referred to in the literature as the sillimanite group. These minerals, while of the same empirical chemical formula, differ crystallographically. Two of them, andalusite and sillimanite, are orthorhombic in crystallization, forming somewhat similar crystals which however, can be differentiated by the accurate measurement of their interfacial angles. The third mineral, cyanite, is triclinic, having a typical crystal form and certain very distinctive physical properties. The optical constants of these minerals, however, allow complete differentiation to be made.

GEOLOGICAL ASPECT OF THE TRIMORPHISM OF $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$

Inversion in dimorphous or trimorphous groups of minerals may bear an important relation to the conditions during the formation of the rocks in which they occur. In fact, inversion has sometimes been interpreted as indicating that rocks containing these minerals must have been formed below certain temperatures. This is true of the minerals of the sillimanite group. For example, Vernadsky¹ concludes, as a result of his experiments, that cyanite must have been formed at a temperature not exceeding 1330°C . However, great pressures are almost certain to accompany the rock-forming processes under which the minerals of the sillimanite group are produced. Furthermore, Vernadsky does not appear to have considered the probable effect of these pressures upon the modification of polymorphous minerals.

From the geological standpoint, the type of rocks in which these minerals occur leaves no doubt that these minerals have been formed under different conditions and that they therefore might be expected to react differently when heated. For example, sillimanite is frequently found near the contact of igneous intrusions with clay rocks, while farther away from the contact and in the same rock andalusite is sometimes noted. In nature, sillimanite is apparently more stable than cyanite and andalusite toward heat. This has also been observed to be the case under the artificial conditions of the laboratory.

On the other hand there appears to be ample evidence that great pressure is an important factor in the formation of cyanite. Van Hise² believes that cyanite is formed in the zone of anamorphism,

as a result of several possible reactions, such as the combination of corundum, diaspore, or gibbsite, with quartz. In every case there is a marked increase in specific gravity during the change. This is due in large measure to the great pressures exerted in the zone of anamorphism. The greater specific gravity of cyanite (3.6, the highest of the sillimanite group) also indicates that it has been formed under higher pressures than the other two members of the group. According to Van Hise, the mineral formed under greatest pressure should have the most closely packed molecules and hence the greatest amount of substance per unit volume, or the highest specific gravity.

Moreover, the type of rocks with which it is usually associated is another indication that cyanite is formed under greater pressures than sillimanite or andalusite. Cyanite is usually associated with mica or quartz-mica schists which represent some of the most intensely metamorphosed, folded, or compressed rocks.

On the other hand, if the results of laboratory experiments are accepted, cyanite is the least stable toward heat and was formed at the lowest temperature of any of these minerals. This, however, would be a rather bold statement to make without qualifications, especially in view of the meager state of our experimental knowledge of the effect of high pressure upon the formation of minerals.

INDUSTRIAL ASPECT OF THE INVESTIGATION

A crystalline constituent having optical properties very similar to sillimanite has been observed as one of the components of many ceramic wares for a long time. This constituent has usually been referred to as "artificial sillimanite." It was also a commonly known fact that the good qualities of many porcelains were due, at least in part, to the formation of this compound. Accordingly, the development of any method or the use of any material which increases the amount of this compound in the ware necessarily becomes of great value in industrial practice.

For some years, therefore, the manufacture of special types of porcelain has tended toward the formation, during burning, of an increasingly higher content of "artificial sillimanite." Bowen and Greig³ have recently shown, however, that its composition is not the same as natural sillimanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), as previously supposed, but rather, is $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Their work showed that the two compounds are not only similar chemically but also strikingly similar optically.

"Artificial sillimanite" as produced in ceramic ware usually results from molecular changes taking place in clay under the influence of heat and various fluxes. The highest content of "sillimanite" has been developed by introducing into the unfired body artificially prepared "sillimanite" in the form of the product of direct fusion or of a calcine—a mixture of clay, alumina and fluxes heated to a temperature of about 1500°C . Although this method has been in use for several years in the manufacture of spark plug porcelains, it was, of course, an expensive way to obtain the desired end.

In order to eliminate the necessity of making an "artificial sillimanite" to be introduced into the body, the logical procedure was to attempt to employ one of the natural Al_2SiO_5 compounds; namely, andalusite, cyanite, or sillimanite. However, the difficulty of obtaining any of these minerals in sufficiently large quantities and in a pure state was not overcome until recently when a large deposit of andalusite was located in California. It was then possible to substitute the natural material for the "artificial sillimanite." Undoubtedly, andalusite will be used in the future for other purposes as well.

As a result of the discovery of this new deposit, a knowledge of the temperatures or points at which the different members of the sillimanite group break down is important from the industrial standpoint in three ways.

First, it is desirable to know in each instance, what products are formed as a result of the breakdown of these minerals. This must be known in order to approach other problems more intelligently.

Second, it is also important to know (a) at what temperature decomposition is complete; (b) whether this point is reasonably stationary and the breakdown sharp; (c) whether the breakdown is slow and persists over a range of temperature.

Third, because of accompanying volume changes in the material at its decomposition point, these changes as well as the actual point of breakdown are important. In order that volume changes may be fully stabilized it is necessary to carry the firing of the ware well beyond the decomposition point, especially if the volume change is large and takes place slowly.

PURPOSE OF THE INVESTIGATION

The purpose of the present investigation is not to establish the exact temperatures at which andalusite, cyanite, and sillimanite

undergo change but rather to establish, first, the nature of the resulting product; second, the points at which decomposition takes place, and whether this decomposition is a sharp change or covers a range of temperature; third, the character of the accompanying volume changes. Any of these changes, when produced under industrial conditions, may take place at quite different temperatures than under the more exactly controlled conditions of the laboratory devoted to pure science.

HISTORICAL

A review of the literature reveals the fact that the investigations of the effect of heat upon minerals of the sillimanite group range from simple descriptions of the loss of color of the minerals when heated in the blowpipe flame, to various attempts to form the minerals synthetically. The most recent work of this kind is that of Bowen and Greig upon the revision of the system $\text{Al}_2\text{O}_3\text{-SiO}_2$ and the true nature of the compounds formed in the breakdown of sillimanite.

Apparently, no attempt has been made to correlate the changes involved with practical ceramics except in the work of Bowen and Greig. This is no doubt due to the fact that only quite recently have any of the minerals of the sillimanite group been used in the manufacture of ceramic ware. To be sure, the presence in ceramic bodies of what has been called sillimanite has been known for a long time, but this substance has developed as a by-product of the molecular decomposition of clay and has recently been shown by Bowen to be not "sillimanite" but actually a compound of the composition $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. For some years so-called "artificial sillimanite" has been manufactured from its oxides or from clay for subsequent use in ceramic ware⁴. This "sillimanite," however, is a synthetic product which should not be confused with the natural minerals.

METHODS USED AND THE CHANGES INVOLVED

In the study of the effect of heat upon minerals of the sillimanite group, three general methods of attack appear to have been used. These methods may be designated as physical, physical-optical, and physical-chemical-optical. A fourth method (chemical-optical) does not appear to have been used in investigations of changes in the natural minerals although it has been used extensively in the

study of artificially formed "sillimanite." Vernadsky¹ summarizes excellently the various attempts of investigators up to 1889.

PHYSICAL METHOD—This represents the earliest type of study and consists largely in simply recording observations of the loss of color and of the whitening effect of minerals when subjected to the blowpipe flame. This, of course, represents a very crude method of determining what changes had taken place; in fact, there seems to be no evidence that there was any serious effort among the earliest observers to follow the matter further.

According to Vernadsky, Saussure,⁵ who first found and described cyanite, observed that needles of cyanite, "losing to fire their color, whatever it may be, change to a dull white. They show a granular texture which renders them somewhat fragile." Many others make practically the same statement. Some ascribed the change to the decomposition of pigments and minerals included in the cyanite. Laugier⁶ and Erdmann⁷ reported losses in weight, sometimes as high as 0.61 per cent. Vernadsky confirmed this and interpreted the loss in weight as possibly indicating that the change may be due, in part, to the loss of some volatile constituent.

Many mineralogists record that andalusite does not lose its original compactness but simply whitens. The same is true of sillimanite.

PHYSICAL-OPTICAL METHOD—This method makes use of alterations taking place in the physical properties, such as hardness and specific gravity, under the influence of heat. These alterations are further supplemented by changes in optical properties.

Vernadsky used a method of this character in his work on cyanite. He found, first, that the average hardness of the mineral increased slightly; second, the specific gravity diminished markedly; third, the fragments showed distinct changes in optical properties. Curiously enough he does not appear to have observed the optical property which is generally considered most important of all: namely, the index of refraction. As a result of this work Vernadsky was able to make the statement that "heated to a determined temperature (about 1200-1330°C), cyanite changes to another mineral which is probably sillimanite." Apparently he had no way of accurately controlling the temperature in these experiments; hence the wide range of temperature mentioned. He also states that sillimanite, and probably also andalusite, is stable at this temperature.

PHYSICAL-CHEMICAL-OPTICAL METHOD—Much credit for the development of this method as a means of investigation belongs to the staff of the Geophysical Laboratory of the Carnegie Institution. The method is essentially synthetic. It involves building up the various binary and ternary compounds from their oxides, and determining all important optical and physical properties, such as melting points of compounds and eutectics, dissociation points, inversion points, and so forth. Thus, the effects of variation in temperature and chemical composition are not only very accurately controlled but they are also supplemented by petrographic-microscopic examination.

Although this method was originally designed as a basis for further detailed study of petrologic problems from the standpoint of pure science, experience has shown that many of the methods developed and the results obtained by the above investigators can be applied to industrial, especially ceramic, problems either in explanation of existing conditions or as aids in research. Their work on the system $\text{Al}_2\text{O}_3\text{-SiO}_2$ has an important bearing in this connection.

One of the earliest investigations using the physical-chemical-optical method was conducted on the system $\text{Al}_2\text{O}_3\text{-SiO}_2$.⁸ The results of this work seemed to indicate that there was only one compound of Al_2O_3 and SiO_2 ; namely, $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, corresponding in most of its optical properties to the natural mineral sillimanite. Certain minor discrepancies somewhat difficult of explanation were observed. Thus, it was never possible to obtain the compound in a perfectly pure state, small amounts of glass always being present. Also, the refractive indices of the artificial crystals were distinctly lower than those of the natural mineral. Owing to the fact that chemically pure oxides were used, the observed optical properties were probably assumed to represent the true constants of the synthetic compound $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, although they were quite different in some respects from those of natural sillimanite. Variations in the natural mineral were thought to be due to impurities. The presence of glass was explained by the high melting point of the compound, since, because of the high temperature at which it began to crystallize and on account of the apparently rapid rate of crystallization, some glass might easily be included between the fibrous crystals.

At the same time these investigators verified Vernadsky's statement that at high temperatures both andalusite and cyanite

undergo changes to another form, probably to sillimanite. The exact temperatures of the changes were not definitely determined, except that they are somewhere between 1150° and 1500°C . Various fluxes apparently decomposed the minerals before the change took place. They were not, however, able to verify the statement that when andalusite undergoes this change an evolution of heat occurs.

The work on the system $\text{Al}_2\text{O}_3\text{-SiO}_2$ was quite generally accepted until recently when Bowen and Greig, in a revision of this system, showed that the former conception was inaccurate, and that although there was but one compound formed between Al_2O_3 and SiO_2 , it is not $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, but rather $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. From the melt of mixtures of the two oxides in these proportions only one component results, which is entirely crystalline and possesses the optical constants previously assigned to the "sillimanite" of the earlier work on the same system. The establishment of this fact immediately explained the discrepancies in the earlier study, such as the lower refractive indices of the so-called artificial sillimanite and the presence of excess glass in the melt of the 1:1 mixture.

Furthermore, Bowen and Greig showed that at 1545°C . natural sillimanite melts incongruently and breaks down into $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and excess siliceous glass. At the same time they examined the "sillimanite" which had been produced in ceramic ware of various kinds and found that in each case it was not $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ but the new compound $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. Subsequently, this new compound was also found to exist in certain fused argillaceous rocks and was given the name mullite.⁹ Thus, although the compound $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ exists in nature in three different crystalline forms, none of them have yet been produced in the laboratory.

SILLIMANITE AND MULLITE IN CERAMIC WARE

As already pointed out, the presence of a crystalline compound, having properties very similar to those of sillimanite, has been recorded in ceramic literature for about fifty years. Since its presence was first noted the occurrence of this compound in ceramic bodies has been studied from many angles. Its importance in lending valuable properties to the ware has become recognized more and more until recently a microscopic description of a ceramic body was not considered complete without some reference to the so-called sillimanite.

Behrens¹⁰ was apparently the first to make a microscopic study of porcelain, the results of which were published in 1873. He stated that the groundmass of molten feldspar undergoes devitrification, and that the material which separated from the groundmass dissolved in hydrofluoric acid less readily than the quartz and glass present. He did not identify the crystals, but his description of their insolubility suggests crystals of "sillimanite."

In a microscopic study of porcelain, Hussak, in 1889,¹¹ described the presence of needle-like crystals, very minute and weakly, doubly refracting, resembling sillimanite. Mellor,¹² in 1907, reported "sillimanite" in Chinese and Berlin porcelains.

Plenske,¹³ in an elaborate study of porcelains published in 1908, noted that porcelains could be divided into groups according to the presence or absence of crystalline products in the groundmass. Furthermore, he observed that "sillimanite" might also be present in masses of exceedingly minute grains which were apparently amorphous. Plenske also believed that the crystalline "sillimanite" was formed by devitrification of the glassy groundmass.

Zoellner,¹⁴ also in 1908, identified optically the occurrence of "sillimanite" in porcelain, and also separated the crystals by hydrofluoric acid. He found that the ratio of $\text{Al}_2\text{O}_3:\text{SiO}_2$ was 1:1. He believed that the "sillimanite" was formed by a molecular change in the clay in the body and not through devitrification.

More recently, in 1916, Klein¹⁵ made a detailed study of various types of porcelain and the relation of the development of "sillimanite" in them to the temperature of burning. Riddle,¹⁶ in 1919, also described the presence of "sillimanite," and its relation to various fluxes and fine grinding. Of recent years reports of the development of "sillimanite" in porcelains have become very numerous.

"Sillimanite" has also been reported in other ceramic bodies besides porcelain. In 1890 Vernadsky¹⁷ called attention to its formation from the heating of clay. In 1919 Cox¹⁸ claimed to have found it in fire clay exposed to a high temperature for a long period, although the chemical analysis which he gave did not indicate a ratio of 1:1 for the constituent oxides but was more nearly 3:2; namely, that of mullite. At various times Mellor¹⁹ has reported its formation in fire brick. Many references might also be given in which its presence in glass is reported. In these cases its formation is believed to be due to the decomposition of clay from the tank or pot walls by the glass.

However, as already mentioned, it remained for Bowen and Greig to point out that the "sillimanite" in all the bodies examined by them was not of the composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, but $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, now called artificial mullite. They were also fortunate in obtaining from an outside source some well crystallized $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which was used to measure accurately both the crystallographic and optical constants and to show its very close similarity to natural sillimanite.

METHOD USED IN THE PRESENT INVESTIGATION

Owing to the accurate and detailed information available on the compounds developed in the system Al_2O_3 - SiO_2 as worked out at the Geophysical Laboratory, the method used for the preparation of the samples and later identification of the resulting products was comparatively simple, involving four steps as follow:

1. Powdered samples of the raw materials were first fired to predetermined temperatures in open crucibles.
2. A careful petrographic-microscopic examination of each of these burns was made, using the method of immersed grains.
3. The crystalline products formed from andalusite and cyanite were analyzed chemically, affording evidence in addition to the work of Bowen and Greig on sillimanite.
4. Determinations were made of the changes in specific gravity between the unfired and fired minerals.

METHOD OF FIRING

The kiln in which the minerals were burned is a large laboratory kiln designed by the Champion Porcelain Company for research work and for the accurate reproduction of conditions in full sized kilns. It is of the down-draft type.

In overall size it is 8 feet high, 6 feet wide, and 4 feet 6 inches deep. The chamber is 3 feet 6 inches high, 3 feet 6 inches wide, and 1 foot 6 1/2 inches deep, and has a capacity of seven 15-inch by 5-inch saggers. Thermoelement pyrometer control is provided through several openings. Cone 32 may be fused in this kiln (about $1705^\circ\text{C}.$).

The minerals were fired in small open crucibles, each containing about five grams of material. Two series of firings were made, after the manner of draw trials. The first series of drawings was started at cone 8 and continued every two cones thereafter, inclusive of cone 16.

Orton cones were used and a definite rate of heating was followed in firing the samples. It should be stated here that standard pyrometric cones do not always indicate a definite temperature as does a thermocouple. According to conditions under which the heating takes place, they may register higher or lower than the actual temperature. They are useful, however, in indicating approximately the temperature reached. For example, cone 10 may bend over until its tip touches the base upon which it rests or be "down" at an actual indicated temperature of $1340^{\circ}\text{C}.$, whereas the temperature at which it should come down theoretically is $1330^{\circ}\text{C}.$ Likewise, other cones may not register the true temperature.

These anomolous conditions result from the fact that the fusion of a standard pyrometric cone involves viscosity and other factors as well as temperature, and therefore indicates heat-work. On this account the ceramist prefers the cone to the thermo-element in actual practice, since the cones show that a certain amount of work has been done. Therefore, since the purpose of this investigation is to obtain the reaction temperatures under working conditions, all temperatures will be expressed in cones. The ceramist uses the thermo-element mainly to indicate whether the temperature is rising, falling, or remaining stationary.

According to the standard scale, cone 1 has a fusion point of $1150^{\circ}\text{C}.$ and each succeeding cone is $20^{\circ}\text{C}.$ higher. The following table indicates the theoretical fusion temperatures from cones 10 to 15.

Cone 10	1330°C
11	1350
12	1370
13	1390
14	1410
15	1430

The microscopic examination of the firings showed that no changes were to be observed in the minerals below cone 11, and, further, that in andalusite and cyanite the changes were completed between cones 12 and 14. Sillimanite, however, showed no decomposition even at the highest temperature.

Having thus established the upper and lower limits of the changes in andalusite and cyanite, a second series of draw-trials was made from cones 10 to 15 inclusive, with samples taken at every cone. It was on these samples that the petrographic-microscopic examinations described later were carried out.

OBSERVATIONS ON THE MATERIAL USED

A. ANDALUSITE

The andalusite which was used in these firings came from the mine owned by the Champion Porcelain Company and located on White Mountain, of the Inyo Range, Mono County, California. A complete description of the crystallography and mineralogy of this andalusite has been given elsewhere.²⁰

Since the andalusite, as received from the mine, is in the form of large fragments, it was necessary to crush it and then to grind the coarse granules without water to a fine powder in a pebble mill. As it was not desired to use the material in a body, and as grains of any size could be studied on the microscope slide, no attempt was made to screen and size it. The powder consisted of about 80 per cent andalusite with minor amounts of pyrophyllite, mica, corundum, and rutile.

THE EFFECT OF FIRING

The above powder, after being fired as previously indicated, was subjected to a careful petrographic-microscopic examination with results which follow.

At cone 10 the only apparent outward change is a slight consolidation of the powder into a firm but quite brittle mass. The microscopical examination shows no change in the andalusite grains. They still remain clear and retain all their original optical properties.

The plates of mica have decomposed into masses of exceedingly minute rounded grains embedded in a glassy matrix, and are quite similar in appearance to the products of the breakdown as it first occurs in kaolin upon hard firing. These granular masses show no double refraction and both constituents are too fine grained to identify.

At cones 11 and 12 there still is no outward change in the appearance of the firings, nor is there any change in the optical properties of the andalusite grains. Due to the higher temperature of firing, the plates of mica show the grains resulting from the breakdown to be somewhat enlarged. Some of these grains are slightly elongated, the long direction being perpendicular to the original cleavage of the mica. Although they are still too minute for complete identification, their optical elongation can be determined as negative. (Figures 1 and 2).

With an increase to cone 13, the mass in the crucible is a distinctly firmer body than in previous burns, a slight amount of sintering having taken place.

Microscopically, the andalusite also is noticeably altered, about half the grains showing the changed character. As is to be expected, most of the smaller grains are decidedly altered while the larger ones may be only partially affected and even in some cases entirely unaffected. The change in the andalusite fragments is apparently due to a breakdown into two components. One of these is crystalline and more abundant, while the other is a glass and minor in amount.

The crystalline component occurs as elongated crystals parallel to each other throughout the whole grain where it is completely decomposed, so that extinction between crossed nicols is complete over the whole grain at the same time. Optically, the indices of refraction are, $\gamma = 1.657$ and $\alpha = 1.643$. The elongation is positive. On account of the small size of the crystals, other optical properties could not be determined. These facts indicate that the crystalline compound formed is artificial mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, described by Bowen and Greig, and which they determined to be the decomposition product resulting from the heating of natural sillimanite above 1545°C . As already indicated, this compound, heretofore supposed to be artificial sillimanite, was also found by them in ceramic ware. (Figures 3 and 4).

The second component is isotropic in character and non-crystalline as far as can be determined. It is apparently a glass. Its refractive index is slightly variable, depending probably upon the character of the impurities present, which have been taken into solution. In general, the index is near 1.54. As pointed out by Bowen and Greig, this glass is probably very siliceous in composition.

As previously mentioned, not all of the grains are decomposed to this mixture of crystals and glass. The change can sometimes be observed at an intermediate stage where grains show a fringe of parallel crystals around the outer edges with an unchanged center. The crystals in the fragment are not formed as radiating crystals but they are parallel throughout, without regard to the part of the grain in which they occur. The border consisting of crystals and glass does not have a definite boundary but passes irregularly and imperceptibly into unaltered andalusite at the center. Of interest also is the fact that the crystals which have formed in the andalusite grain are of opposite optical orientation from the original grain. (Figures 5 and 6).

Heated to cone 14 the powdered mass shows an increased firmness but is still not solid. The microscopic examination indicates that the decomposition is complete in all of the smaller grains of andalusite and in most of the larger ones. The smaller grains show crystals of mullite which are slightly larger than those formed at cone 13. A few of the largest grains still possess unchanged centers with crystal borders, but these are uncommon. (Figure 7).

At cone 15 it is apparent that every grain is decomposed, even the largest and coarsest.

B. CYANITE

The cyanite used in these firings was obtained from Charlotte Court House, Virginia. Although the material is composed largely of cyanite, considerable amounts of quartz and a little muscovite mica are present as admixtures. Before being used commercially the crude material would probably require treatment to eliminate most of the quartz and mica, but for the purposes of the present work this was unnecessary.

Before firing, the material was ground to a powder but was not screened to any definite size, following the same procedure as with andalusite. This, however, did not affect the results as grains of the same size were considered in each case.

THE EFFECT OF FIRING

Since all three members of the group were fired together, the conditions were the same for cyanite as those described for andalusite.

At cone 10 the powder retains its slightly bluish green color. The cleavage surfaces of the larger grains can still be seen to be smooth and bright. The mass shows a very slight cohesion such as was noted in the corresponding burn of andalusite.

When examined microscopically no change in the optical properties of the fragments can be detected. They are still the same flat, straight-edged fragments, sometimes showing step-like terminations and cleavage cracks as in the unburned material. (Figures 8 and 9). The small amounts of mica present appear the same as in the andalusite burn at cone 10.

When heated to cone 11 there is still no outward change in the powder. Cleavage surfaces are bright and smooth for the most part, and the faint bluish color is present.

Slight changes in microstructure appear to have commenced. Some fragments show the development of a few scattered fibrous crystals. These are similar in appearance to those formed in anda-

lusite but are too far underdeveloped to make identification certain. Cleavage cracks in the fragments are somewhat more numerous, especially those perpendicular to the length of the grain. These are no doubt due to the expansion of the fragments under the influence of increasing temperature. The above evidence, though slight, suggests that a point is being approached where marked changes will take place.

When fired to cone 12, the powder loses some of its color and assumes an external appearance slightly different from that of the preceding burn. Smooth, glistening cleavage surfaces are also less common.

The microscopic decomposition is far more pronounced than would be suspected from the appearance of the powder alone. The fragments have broken up into irregular areas of crystals showing double refraction but these areas do not extinguish together. Only the largest grains show unchanged centers with altered borders. The small fragments show fibrous areas of elongated crystals, these areas being oriented in all directions and forming interlocking aggregates of needles; hence, the fragments have a peculiar mottled appearance between crossed nicols. This is in distinct contrast to the marked parallelism of the crystals developed from andalusite. The crystals formed from cyanite have between them, as in andalusite, an amorphous, glass-like substance. The refractive indices of the crystals are: $\gamma = 1.655$ and $\alpha = 1.642$. The glass has an index of 1.54. The elongation of the crystals is positive. As in the case of andalusite, other optical properties are not obtainable because of the small size of the crystals. Thus, from all indications optically, both the crystals and the glass are the same components as are formed during the breakdown of andalusite. (Figures 10 and 11).

At cone 13 there is a very pronounced external change in the powder. It becomes dull white in color and loses much of the slight cohesion it previously had. A large fragment burned along with the powder became dull white in color and very brittle, breaking down into many fragments during burning. These fragments when touched lightly, in turn crumble to a fine powder. This is due as pointed out by Vernadsky¹ to a pronounced expansion in volume and a decrease in specific gravity accompanying the change in constitution.

The microscopic examination reveals that the breakdown, which was well started at cone 12, has been entirely completed on the largest fragments. It shows, however, a more complete and definite

development of variously oriented areas of mullite crystals and glass, and also that in many instances the firing to the higher temperature has served to increase the size of the crystals.

No further marked change from cone 13 is apparent either externally or microscopically, at cones 14 or 15. In each case there is a tendency toward further growth in the size of the mullite crystals formed.

C. SILLIMANITE

The sillimanite used in firings covering the same range as those of andalusite and cyanite was obtained from a recently reported Indian deposit, presumably from the Khasia Hills of Assam.²¹

It was used in the form of a fairly coarse powder with a grain size somewhat greater than the cyanite. The material was rather pure, consisting of irregular grains with an internal fibrous structure. Only a small amount of muscovite mica, quartz, and iron oxides were present as impurities.

THE EFFECT OF FIRING

The firing was carried out in the same manner as for the other two members of the group.

As Bowen and Greig have pointed out, sillimanite does not decompose until a temperature of 1545°C has been reached, and since the maximum cone of the present series was only cone 15, no changes in structure were anticipated but the mineral was included mainly for the purpose of completeness.

At all cones including cone 15 the material remained a loose, incoherent sand, no hint of sintering being observed. There was no external change in the grains.

Upon microscopic examination no decomposition could be detected even at cone 15, the grains at all times retaining the optical properties of sillimanite, losing none of their original structure, and showing no signs of a breakdown similar to the other two members of the group.

CHEMICAL COMPOSITION OF ARTIFICIAL MULLITE

Although Bowen and Greig did not analyze the artificial mullite crystals which were developed by heating natural sillimanite, they did show that these crystals had the same optical properties as pure artificial mullite. They also separated and analyzed crystals

produced in the burning of various types of ceramic ware, and showed that these, too, were the same as mullite except that small amounts of Fe_2O_3 and TiO_2 which had been taken into solid solution increased the indices of refraction of the crystals noticeably and also produced a violet or pink pleochroism.

Since the optical properties of the crystals formed by the dissociation of andalusite and cyanite are very similar to those of mullite, chemical analyses of them were made. The chief obstacle encountered in determining the composition of these crystals was due to their very minute size. This not only renders it difficult to free them from the admixed silica glass but appears to make the crystals themselves very susceptible to decomposition in cold hydrofluoric acid.

In the preliminary examination the crystals were exposed to cold hydrofluoric acid for one week, the fired material having been previously ground to a very fine powder. This treatment resulted in the complete decomposition of the crystals as well as the silica glass. Finally, the method used by Vernadsky and adapted by Bowen⁹ was followed, allowing the powder to stand in 25 per cent hydrofluoric acid over night at room temperature. After the crystals were freed from excess acid by repeated decantations, they were finally filtered off. Treated in this manner both the andalusite and cyanite burns gave fairly pure residues of mullite crystals. The former contained appreciable amounts of corundum, some undissociated andalusite, rutile, and a little glass, while the latter showed a slight decomposition of the crystals and a very little corundum.

The results of the chemical analyses given in the table below confirm the optical evidence.

	COMPOSITION OF MULLITE CRYSTALS FORMED FROM		
	Andalusite	Cyanite	Theoretical for $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
SiO_2 (corrected)	31.98	27.37	28.2
Al_2O_3 "	68.02	72.63	71.8
Corundum	1.50	1.39	
Rutile	1.77		

Thus, it is quite apparent that the agreement between the analyses and the theoretical composition is sufficiently close to warrant the composition of the crystals being placed at $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The more siliceous character of those obtained from the andalusite

burn is mainly due to the presence of some andalusite which was not entirely decomposed during burning. There does not appear to be any method at present to determine andalusite separately, as can be done for corundum and rutile. The low SiO_2 in those from the cyanite burn is probably due to slight decomposition previous to analysis.

Attention is called particularly to the fact that TiO_2 is present as rutile and is not in solid solution in the mullite. This accounts for the fact that the indices of refraction of the mullite crystals do not vary appreciably from those of pure synthetic mullite, nor do these crystals exhibit the characteristic pleochroism of mullite containing TiO_2 .

CHANGES IN SPECIFIC GRAVITY AS A RESULT OF FIRING

While very little change in volume was observed in the andalusite powder at its dissociation point, that which accompanied the dissociation of cyanite was very pronounced. This was more apparent when a comparison of the unfired and fired powders was made, as shown in the following table. The standard pycnometer method was used.

	Specific Gravity	
	Unfired	Fired to cone 15
Andalusite	3.29	3.20
Cyanite	3.59	3.09
Sillimanite	3.15	2.92

It is quite apparent that cyanite is most affected as a result of heating, while sillimanite is affected much less and andalusite least of all.

The decrease in specific gravity in andalusite and cyanite is attributable directly to the dissociation. In sillimanite, however, no dissociation is apparent microscopically. The change, therefore, would seem to be due to the production of fine microscopic or submicroscopic cracks caused by the natural thermal expansion with increasing temperature or, perhaps more likely still, to volume changes in the associated minerals which were present in small amounts.

SUMMARY OF CHANGES DURING FIRING

The results of the changes in constitution, microstructure, and volume of the members of the sillimanite group when fired up to cone 15 may be briefly summarized as follows.

ANDALUSITE—From the evidence furnished by the petrographic-microscopic examination of the various burns it is certain that, under the conditions detailed, andalusite breaks down rather abruptly at cone 13, yielding a mixture of mullite and a siliceous glass. The resulting structure is one of parallel crystals extending throughout the whole area of a grain of the mineral, with interstitial glass. If the grain be rather large, the center may be unchanged with a fringe of crystals and glass around the outer edges.

The optical orientation of the crystals thus formed is opposite to that of the original grain. Firing to higher cones serves to enlarge the size of the crystals somewhat and to complete the breakdown of the larger grains. The volume changes are small, only a slight expansion taking place.

CYANITE—The change in cyanite does not appear to be as abrupt as in andalusite. The increase in the cleavage cracks crossing the length of the fragments and the incipient formation of fibrous crystals seem to indicate that at cone 11 a point is being approached where marked changes will occur. These changes actually occur at cone 12, but the microscopic changes are more pronounced than the megascopic appearance would indicate.

The same components are formed as in andalusite; namely, mullite and interstitial glass; but these constituents have developed an entirely different structure and relationship to the original grain from that observed in the andalusite burns. They occur in irregular areas, each grain frequently containing several crystal areas. In any one of these areas the crystals may be parallel to each other but of decidedly different orientation from that of the other areas in the same grain. Adjacent areas interlock more or less with each other.

There is a very marked increase in volume at the dissociation point, much greater than that which takes place in andalusite.

SILLIMANITE—Sillimanite shows no change megascopically or microscopically, inclusive of cone 15. This is in complete accord with the observations of Bowen and Greig.

The volume change is not as great as in cyanite, but is greater than that of andalusite. Because no dissociation is observable microscopically, it seems probable that it is due in part to the formation of cracks produced by thermal expansion or to the associated minerals.

THE SIGNIFICANCE OF THE CHANGES

MONOTROPISM AND CERAMIC WARE

It has been shown that the minerals of the sillimanite group break down at certain points with accompanying mineralogical and volume changes. This brings up a factor which is of extreme importance from the practical standpoint, that of monotropism and its relation to ceramic ware.

If minerals undergo change or inversion to a different crystalline substance of identical chemical composition when heated below their melting or disintegration points, the change may be of two kinds; that is, it may be a temporary or a permanent change. In the case of a temporary change, where the original crystalline condition returns when the mineral is cooled, it is referred to as enantiotropic. If the change is permanent, the mineral is said to be monotropic in its reaction toward heat. In either case the change may be rapid or slow, a quality inherent in the substance itself.

THE SILICA MINERALS—A classic example of enantiotropism and one which has a distinct bearing on the ceramic industry is that of the mineral quartz.²² When quartz is heated or cooled a number of crystalline forms (seven in all) may be produced, depending upon the temperature and time factors. The more important of these inversions may be conveniently expressed in the following table. The inversion from the α - to the β - form of the same mineral is usually rapid while the change from one mineral to another is much slower.

α -quartz \rightleftharpoons β -quartz	570-575°C, rapid
β -quartz \rightleftharpoons β_2 -tridymite	870° , slow
β_2 -tridymite \rightleftharpoons β -cristobalite	1470° , slow
β -cristobalite \rightleftharpoons glass	1710°

In the absence of a flux the change from β_2 - tridymite to β - cristobalite is easier than that from β -quartz to β_2 -tridymite; hence, we frequently find that β -quartz may invert to β -cristobalite without passing through the β_2 -tridymite stage. This is what happens ordinarily in the original burning of silica bricks. The tridymite develops in them in large measure subsequent to, rather than before, the formation of cristobalite, under conditions of long continued heating at some temperature above 870°C and below 1470°C.²³ Moreover, the greatest expansion in silica bricks takes place when quartz inverts to one of the tridymite or cristobalite forms. Thus, although the silica minerals are enantiotropic, the

reversion is so slow that once inversion has been accomplished to tridymite or cristobalite, the ware takes on practically a monotropic character.

THE SILLIMANITE GROUP MAY BE CONSIDERED AS ESSENTIALLY MONOTROPIC—As has been previously shown, when any of the members of the sillimanite group are subjected to heating to certain temperatures which vary with the different minerals, each one breaks up into two substances. One is artificial mullite of the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The other is a glass of a highly siliceous nature occurring as interstitial matter between the crystals. The crystalline substance formed in each case apparently has the same composition. This is also true of the glass. Strictly speaking, therefore, we cannot say that the members of the sillimanite group are monotropic in character because they break down and yield two substances differing in chemical composition from that of the original mineral. However, neither under conditions of slow or rapid cooling do these two compounds unite to form one compound having the properties of any member of the sillimanite group but they remain unchanged. Therefore, for all practical purposes, from the ceramic standpoint, the members of the sillimanite group may be considered as monotropic toward heat. Although consisting of two compounds, the end product is the same in all cases.

THE PRACTICAL SIGNIFICANCE OF THE CHANGES

THE IMPORTANCE OF MONOTROPISM IN CERAMIC WARE—One of the chief requirements of ceramic ware is that it must be monotropic, or practically so, toward heat. This is especially true in the case of refractories. If a ceramic body is not monotropic, the oscillation or alternation of conditions would cause variations in the physical properties of some or all of the constituents of the refractory or other body to meet those conditions. Thus, undue expansion or contraction may be produced by a change in mineralogical composition. Hence, the special monotropic character of the sillimanite group, after burning to the cones indicated, is particularly valuable to the ceramist.

THE IMPORTANCE OF VOLUME CHANGES—In this connection, also, the volume changes occurring in andalusite, cyanite, and sillimanite may be of as great significance as the actual mineralogical changes in the practical use of these minerals. Thus, if cyanite were used in a body, it would show a large and sudden expansion at

cone 12 and great strains would be set up, accompanied by the production of cracks. The result of this would be a weak, porous, and "punky" body, as is the case of many silica bricks which have been fired too rapidly. In order to correct this, it would be necessary to calcine cyanite to at least cone 12 previous to its incorporation into a body mix, but this would involve additional expense. On the other hand the interlocking character of the mullite crystals developed from cyanite indicates a structure possessing possibilities of superior mechanical strength, which might be worth the extra effort involved in its preparation.

Sillimanite shows a smaller expansion than cyanite up to cone 15 and would be subject to the same objections given for that mineral, but not to such a great extent. However, a much higher temperature (probably at least cone 20) would have to be used to convert it into mullite and glass.

In contrast to the behavior of cyanite and sillimanite, andalusite shows only a slight expansion up to cone 15 and its decomposition has been accomplished previous to this point; namely, at cone 13. It should be possible, therefore, to introduce it into a body in the raw state without subsequent production of strains. It would probably be advisable, however, to fire any body containing andalusite to above cone 13, if it is desired to convert it into mullite and to absorb incidental strains created at the decomposition point. Bowen and Greig have suggested that owing to the regular structure developed in the breakdown of natural sillimanite where the crystalline phase is external, a body using sillimanite may be mechanically stronger than one using the artificial 1:1 $\text{Al}_2\text{O}_3\text{-SiO}_2$ mixture where the resulting external phase is liquid. This may also hold good in the case of andalusite; namely, that bodies in which it has been used might be stronger mechanically than those using the artificial 1:1 mixture.

Thus, from the standpoint of changes in volume produced by firing, and the development of artificial mullite, andalusite is the most desirable of the three minerals for use in ceramic ware.

CONCLUSIONS

1. Andalusite and cyanite dissociate at high temperatures into mullite and a siliceous glass, both products being the same in optical properties and chemical composition as those resulting from the breakdown of sillimanite as described by Bowen and Greig.

2. Andalusite dissociates at about cone 13, (approximately 1390°C), and cyanite at about cone 12 (approximately 1370°C). The breakdown in each case is sharp and only extends over a small range in temperature.

3. The microstructures developed in andalusite and cyanite below cone 15 are entirely different and characteristic.

4. Andalusite shows only a slight change in volume at its dissociation point, practically no disintegration or expansion being noticeable even in large fragments. Hence, it may be introduced into a body without previous calcination.

5. Cyanite shows a great increase in volume at its dissociation point accompanied by marked disintegration. This is so pronounced that unless calcined at a minimum of at least cones 12 or 13 previous to its introduction into a body, a weak and porous product would result.

6. Due to the interlocking structure of the crystal areas produced in the breakdown of cyanite, it is possible that cyanite might give a stronger body mechanically than one of the same composition made by using andalusite. Previous calcination however, would be necessary.

7. Sillimanite can probably be introduced directly into a body with but little disturbance up to cone 20, but in order to convert it into mullite it would be necessary to fire it higher than cone 20. Furthermore, it would be necessary to fire such a body to a still higher temperature in order to produce one of constant volume.

8. Unless cyanite has been previously calcined, andalusite and sillimanite are more desirable because of the great expansion of cyanite at its decomposition point.

9. Between cones 13 and 15, andalusite should be given preference over sillimanite because decomposition has been accomplished and equilibrium established at cone 13.

10. Finally, the value of andalusite lies (a) in its dissociation point being at a moderate temperature; (b) in the refractoriness of the products of decomposition; (c) in the possibilities of great mechanical strength developed by the structure formed in dissociation; and (d) in its lack of decided volume change at dissociation.

ACKNOWLEDGEMENTS

The writer takes this opportunity to express his most sincere thanks to Dr. J. A. Jeffery and Mr. F. H. Riddle of the Champion Porcelain Company for their hearty co-operation in making the

firings; and to Professor E. H. Kraus for suggestions in the revision of the manuscript.

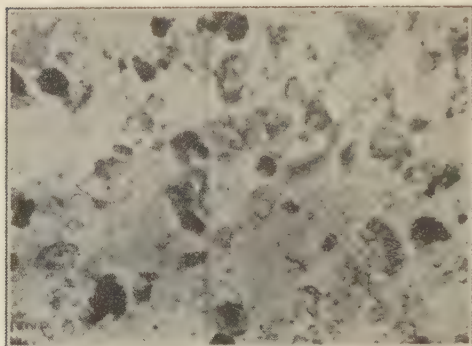


Fig. 1. Andalusite, cone 12. Note the clear unaltered grains. The black grains are mica which has decomposed. Magnification 90.

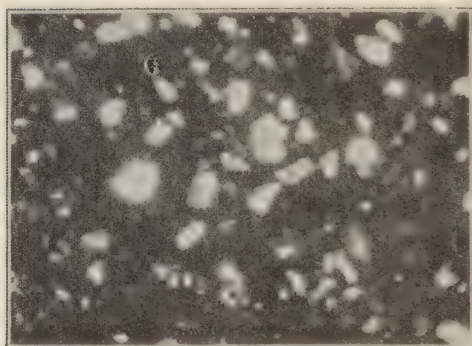


Fig. 2. Same field as Fig. 1 taken with crossed nicols. Note the strong double refraction of the andalusite.

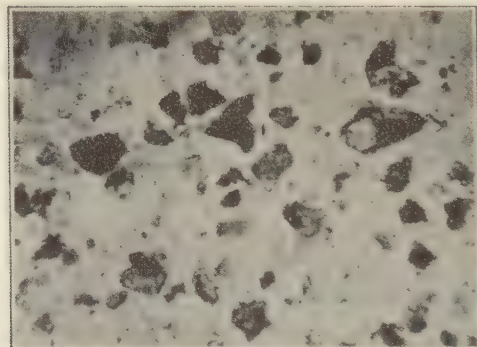


Fig. 3. Andalusite, cone 13. Note that many of the grains are clouded and have a somewhat fibrous appearance due to decomposition with the formation of fibrous crystals of mullite with interstitial glass. Magnification 90.

Fig. 4. Andalusite, cone 13. The grain in the center of the preceding photograph magnified to 315 times, showing the detail of the parallel fibers of mullite extending across the grain.

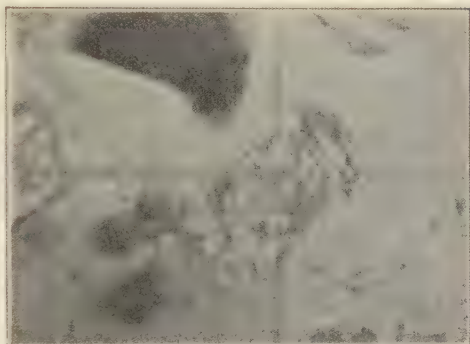


Fig. 5. Andalusite, cone 13. Showing a grain having decomposed border of fibrous crystals and glass, with a clear unaltered center. Magnification 315.

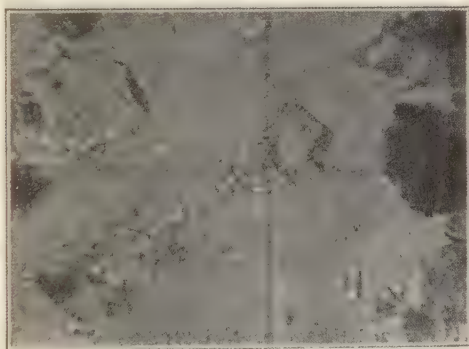


Fig. 6. Same field as Fig. 5 taken with crossed nicols. Note the strong double refraction of the unchanged center and weaker double refraction of the fibrous border.



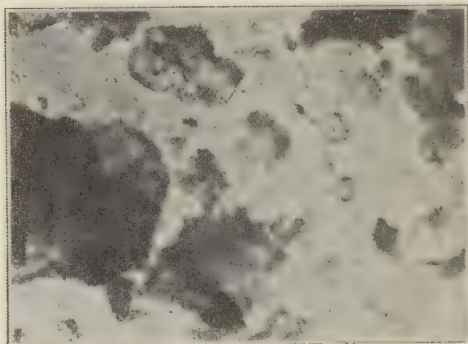


Fig. 7. Andalusite, cone 14. Showing all grains to be decomposed to aggregates of parallel fibers as contrasted to the partial decomposition of some of the grains in the cone 13 burn, Fig. 3. Magnification 165.

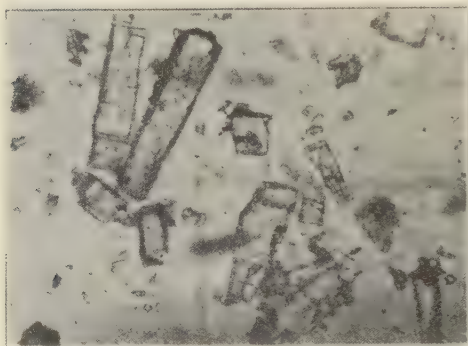


Fig. 8. Cyanite, cone 10. Note the clear undecomposed grains and cleavage cracks. The black grains are mica as in [Fig. 1. Magnification 90.

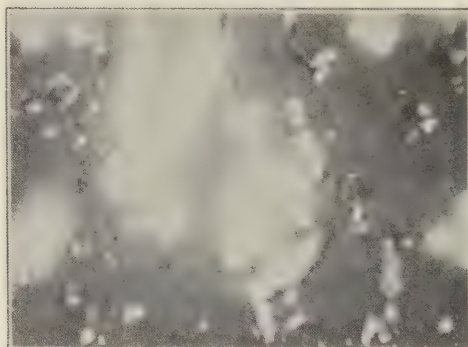


Fig. 9. Same field as Fig. 8, showing the strong double refraction of cyanite.

Fig. 10. Cyanite, cone 12. Showing at high magnification the intimate detail of a grain of decomposed cyanite. Note that the fibrous crystals are not parallel as compared to those in decomposed andalusite (Figs. 3 and 4), but are intricately interlocked. The clear grain is quartz. Magnification 315.

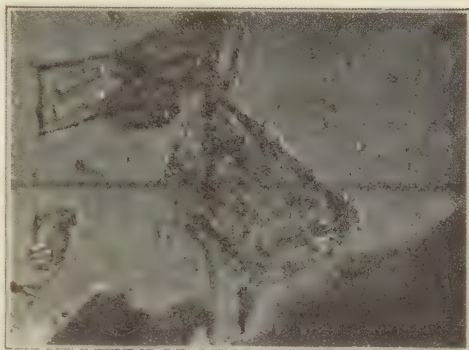


Fig. 11. Same field as Fig. 10 taken with crossed nicols. Note the mottled appearance of the large grain in the center, due to variously oriented groups of fibers. Some are in extinction, while others are light.



BIBLIOGRAPHY

1. W. VERNADSKY: Note sur l'influence de la haute temperature sur le disthene: *Bull. Soc. Fr. Min.*, **12**, 447-56 (1889).
2. C. R. Van Hise: Treatise on Metamorphism. *U. S. Geol. Sur. Monograph* **47**, 381-3.
3. N. L. BOWEN and J. W. GREIG: The system $\text{Al}_2\text{O}_3\text{-SiO}_2$. *J. Am. Cer. Soc.* **7**, 238 (1924).
4. A. V. BLEININGER and F. H. RIDDLE: Special spark plug porcelains. *J. Am. Cer. Soc.*, **2**, 564 (1919).
5. SAUSSURE: Voyage dans les Alpes. Vol. **4**, 84-5, Neuch. (1796).
6. LAUGIER: Analyse de disthene du St. Gothard. *Ann. du Mus.*, **5**, 13 (1804).
7. ERDMANN: Undersokning af några Lerjordssilikater. *Sv. Akad. Vet. Händl.*, **24**, (1843).
8. SHEPHERD, RANKIN, and WRIGHT: The binary systems of alumina with silica, lime, and magnesita. *Am. J. Sci.*, **28**, 302 (1909).
9. BOWEN, GREIG, and ZIES: Mullite, a silicate of alumina. *J. Wash. Acad. Sci.*, **14**, 183 (1924).
10. H. BEHRENS: Ueber das porcellan und einige verwandte entglasserungsproducte. *Pogg. Ann.*, **150**, 386 (1873).
11. E. HUSSAK: Sprechsaal, 153 (1889).
12. J. W. MELLOR: Some chemical and physical changes in firing pottery. *J. Soc. Chem. Ind.*, **26**, 375 (1907).
13. E. PLENSKE: Ueber mikrostruktur und bildung des porzellans. *Tonind. Ztg.*, 1343 (1908); Sprechsaal, **41**, Nos. 20, 21, 22 (1908).
14. A. ZOELLNER: Zur frage nach der chemische-physikalischen natur des porzellans. *Chemische Industrie*, 212 (1908).
15. A. A. KLEIN: Constitution and microstructure of porcelain. *U. S. Bureau of Standards, Tech. Paper*, **80** (1916).
16. F. H. RIDDLE: Further studies of porcelain. *J. Am. Cer. Soc.*, **2**, 812 (1919).
17. W. VERNADSKY: Sur la reproduction de la sillimanite. *Bull. Soc. Fr. Miner.*, **13**, 256-71 (1890).
18. A. H. COX: Note on some South Staffordshire fire-clays and their behavior on ignition. *Geol. Mag.*, **5**, 61 (1918).
19. J. W. MELLOR: *Loc. cit.* (11); Some notes on the action of heat on fire-clays. *Clay and Pottery Industry*, 909-15.
20. A. B. PECK: Note on andalusite from California; a new use and some thermal properties. *Am. Min.*, **9**, 123-9 (1924).
21. Anonymus. Sillimanite: a high grade refractory. *Bull. Imperial Inst.*, **21**, 383 (1923); through *J. Am. Cer. Soc.*, **7**, abstract division, p. 15 (1924).
22. C. N. FENNER: The stability relations of the silica minerals. *Am. J. Sci.*, **36**, 331 (1913).
23. H. INSLEY and A. A. KLEIN: Constitution and microstructure of silica brick and changes involved through repeated burnings at high temperatures. *U. S. Bureau of Standards, Tech. Paper*, **124**, (1919).

THE CRYSTAL STRUCTURE OF SOME METALLIC SULFIDES*

LEWIS S. RAMSDELL, *University of Michigan*

ABSTRACT

By making use of crystal structure as the criterion of isomorphism, argentite, hessite, eucairite, and naumannite are ruled out of the galena group because their structures are entirely different from that of galena. Clausthalite and altaite are isomorphous with galena, as their structures are similar. The isomorphism of the pyrite group is verified, except in the case of smaltite and chloanthite, which gave unsatisfactory data. Covellite and cinnabar are found not to be isomorphous. Cinnabar has a simple rhombohedral structure.

Argentite and acanthite are shown to have identical structures, and hence do not represent distinct mineral species.

Values obtained for the atomic radii of selenium and tellurium from the compounds PbSe and PbTe are Se 1.15 Å, and Te 1.27 Å.

INTRODUCTION

The determination of the structure of a crystal is important in itself, but becomes of much greater significance when the structure can be correlated with chemical or physical properties, or when it has a bearing on certain conceptions which originated before such determinations were possible. Accordingly, in this investigation, not only was an attempt made to determine the structures of some of the metallic sulfides, but also the results so obtained were used as the criterion of isomorphism.

The mineralogist uses isomorphism as a convenient method of grouping minerals which have closely related properties. An isomorphous group is usually defined as one in which the members have analogous chemical compositions and crystalize in strikingly similar forms. Such a definition is capable of varied interpretations. Aside from certain groups where the isomorphism is very evident, it is a matter of opinion as to what compositions can be considered as analogous, or what forms are strikingly similar. In this investigation it was decided to use the crystal structure as the final test of isomorphism. This introduces nothing radically different into our conception of isomorphism. It is merely making use of a fundamental fact rather than a certain manifestation of that fact. The crystal form is ordinarily the outward expression of the inner structure, but if for any reason it furnishes evidence which is not

* From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, June, 1925.

well defined, the isomorphism should be based upon the structure itself.

This investigation covered the sulfides of a number of the metallic elements, and also included the closely related selenides and tellurides, as well as one arsenide and an antimonide. The term metallic sulfide is used in a general sense throughout the paper, and includes these similar compounds.

The equipment used in this investigation was an X-ray Diffraction Apparatus built by the General Electric Company. It is a self-contained unit, consisting of a high tension transformer and a water cooled Coolidge tube, with a molybdenum target. The radiation is rendered practically monochromatic by the use of a ZrO_2 filter. The tube was ordinarily run at about 25 mil-amperes and from 30 to 35 kilovolts, and the exposures varied from 15 to 40 hours. The samples to be photographed were powdered and passed through a 200 mesh screen. In certain cases it was necessary to further grind the sample, and obtain finer material by suspension in water. The powder was placed in a glass tube, made by drawing out thin walled glass tubing to an outside diameter of about 1 mm.

THE GALENA GROUP

This group consists of a series of monosulfides, selenides, and tellurides of lead, silver, and copper, of which the more important members are as follows:

Galena	PbS
Clausthalite	PbSe
Altaite	PbTe
Argentite	Ag_2S
Hessite	Ag_2Te
Eucairite	$(Ag, Cu)_2Se$
Naumannite	$(Ag, Pb)Se$

The reason for including the galena group in this investigation was to determine whether or not the different members have the same structures. According to the theory of space groups it should be impossible for a compound like Ag_2S to have a structure similar to that of PbS. If the structures are different, similarity of crystal form is merely a coincidence, and does not indicate a fundamental relationship. In that case the compounds should not be considered isomorphous.

GALENA

Galena has the NaCl type of structure,¹ although no data have been published. The results secured by means of powder photo-

graphs are shown in Table I, where the spacings of the planes causing the reflections are given directly in Ångstrom units. The specimens used were as follows: (1) a cleavage fragment from an unknown locality; (2) an argentiferous galena from Colorado; (3) a non-argentiferous galena from Kansas; (4) material prepared artificially by precipitation from solution; (5) material prepared artificially by the direct union of the elements. There was no measurable difference between specimens (2) and (3). This was to be expected, for although the one from Colorado was classed as a good silver ore, the actual percentage of silver was not much over 0.1 per cent. The length of the side of the unit cube as determined from the average of the results from the plane 100 (2) was 5.93 Å.

The structure is made up of two interpenetrating face centered cubes, but the diffraction pattern is characteristic of a simple face centered cube arrangement. This is because the reflecting power of the S atoms is relatively so much less than that of the Pb atoms that they are practically negligible, and the pattern is determined by the Pb atoms alone. The theoretical and the observed intensities of the reflections from the different planes are shown in Table II.

CLAUSTHALITE

No specimen of natural PbSe was available, so the measurements were made on artificial material. The results are shown in Table I. It will be noticed that the interplanar distances are a little greater than in the case of galena, for the introduction of the larger Se atoms naturally causes an enlargement of the structure. The length of the cube side was found to be 6.14 Å. The diffraction pattern was quite similar to that of galena, except for some variation in the relative intensities of reflections from corresponding planes, due to the greater reflecting power of the Se as compared with the S atoms. Calculated and observed intensities are given in Table II.

ALTAITE

A specimen of the natural mineral from New Mexico was available but it proved to be Pb(Te, S) rather than PbTe. The spacings were larger than for either galena or clausenthalite, but not as large as would be expected from the introduction of the larger Te atoms. Accordingly, artificially prepared material was measured, with the results shown in Table I.

The pattern obtained was different from those of the two preceding minerals. It indicated a simple cube arrangement rather

than a face centered cube. No reflections were secured from the planes 111, 311, and 331, whereas they were all present for galena and clausthalite, but this does not mean that it possesses a different structure. The Te atom is so much greater in its reflecting power that it cannot be ignored as was the S atom in galena. Both the Pb and the Te atoms must be considered. The effect of two interpenetrating face centered cube lattices, where both are nearly equivalent in reflecting power, is practically the same as that of a simple cube arrangement, with a cube edge only one half as long. Such a cube should give reflections from planes 100, 110, 111, 100 (2), 210, and 211. To make these comparable with the larger cube, the order of reflection would have to be multiplied by two. These planes then become 100 (2), 110(2), 111 (2), 100 (4), 210 (2), and 221(2), and it will be seen in Table I that these are the planes which gave reflections for PbTe. The value for the spacing from the plane 100(2) gives 6.34 Å for the length of the unit cube edge.

Table I. VALUES OF INTERPLANAR DISTANCES IN Å UNITS

Plane	Galena PbS					PbSe	PbTe
	1	2	3	4	5		
100	a	a	a	a	a	a	a
110	a	a	a	a	a	a	a
111	3.42	3.40	3.40	3.42	3.40	3.55	a
100(2)	2.98	2.95	2.95	2.98	2.95	3.07	3.19
210	a	a	a	a	a	a	a
211	a	a	a	a	a	a	a
110(2)	2.100	2.085	2.085	2.100	2.085	2.17	2.26
100(3)	a	a	a	a	a	a	a
221	a	a	a	a	a	a	a
310	a	a	a	a	a	a	a
311	1.795	1.782	1.782	1.790	1.780	1.840	a
111(2)	1.720	1.708	1.708	1.720	1.700	1.760	1.845
320	a	a	a	a	a	a	a
321	a	a	a	a	a	a	a
100(4)	1.490	1.480	1.485	1.485	1.480	1.525	1.600
410	a	a	a	a	a	a	a
330	a	a	a	a	a	a	a
331	1.363	1.362	1.362	—	—	1.40	a
210(2)	1.329	1.328	1.328	—	—	1.360	1.430
211(2)	1.210	1.210	1.210	—	—	1.240	1.310

Explanation of the table.— All possible planes for a cubic structure with spacings greater than that of 211(2) are listed. The letter "a" signifies that no reflection was secured.

Table II. CALCULATED AND OBSERVED INTENSITIES OF REFLECTION

Plane	PbS		PbSe		PbTe	
	a	b	a	b	a	b
111	8.7	1	3.4	4	0.9	0
100(2)	10.0	1	10.0	1	10.0	1
110(2)	9.2	1	8.9	1	8.9	1
311	5.4	2	2.2	5	0.6	0
111(2)	3.7	4	3.7	3	3.7	3
100(4)	2.0	6	2.1	5	2.1	4
331	3.0	5	1.2	6	0.3	0
210(2)	6.3	3	6.0	2	6.1	2
211(2)	5.0	3	4.8	3	4.9	3

Explanation of the table.—The theoretical intensities (column a) were calculated by means of the intensity formula,² and the values were reduced to a scale of ten, so that the most intense reflections have the value 10. In the case of the observed values (column b) no attempt was made to measure the intensities quantitatively. On each film the most intense line (or lines) was given the value of 1, and the remaining lines were arranged in order of decreasing intensity with the values of 2, 3, 4, and so on, with 0 indicating complete absence. It will be seen that the order so obtained agrees closely with the order of the calculated intensities.

This table shows why the diffraction pattern from PbTe is of a different type than those of the other two. The intensities for planes 111, 311, and 331 are very low compared to those of the remaining planes. On a film where the others showed very distinctly, these three would be entirely obscured by the general blackening of the film. The pattern would consist, then, of only the planes 100(2), 110(2), 111(2), 100(4), 210(2), and 211(2). As mentioned before, if the order of these reflections is divided by two, these become the planes characteristic of a simple cube, the length of whose edge has been reduced by one half.

ATOMIC RADII OF Se AND Te

If in a compound selenium or tellurium is partly replaced by sulfur, or if lead is partly replaced by silver, as in the mineral naumannite, the size of the unit cell will be changed. Hence, any measurements as to the size of the atoms must be made on material in which the exact amount of the replacement is known, or on material where there is no replacement. This latter case is much simpler, and the data have been secured entirely from the artificially prepared pure PbS, PbSe, and PbTe.

There is no definite radius for the atom of a given element. In fact, the term "radius" is hardly justified, for it implies that the

atom is spherical. The actual meaning of the term can be explained as follows. As atoms occur in a structure, there is a certain distance between the centers of two adjacent atoms. If the two are alike, half of this distance is referred to as their radius. If they are unlike, a certain fraction of this distance is assigned to one of the atoms as a measure of its radius, and the remaining distance as the radius of the other atom.

If we assume that the S atom in the sulfides has a constant radius, then it is a simple matter to calculate the radii of Se and Te. In the mineral pyrite, FeS_2 , the two S atoms are so placed that they are much nearer to each other than to any of the Fe atoms. This distance of nearest approach is 2.08 Å, so the radius of S is 1.04 Å. In galena, the distance from a Pb atom to a S is 2.96 Å. If 1.04 Å of this distance is assigned to the S atom, then the Pb atom must have a radius of 1.92 Å. Using this value in turn in the two compounds PbSe and PbTe gives 1.15 Å and 1.27 Å as the radii of Se and Te, respectively.

It might be considered that since pyrite and galena have different types of structures, the S atoms would not necessarily have the same radius in the two compounds. In that case the value of 1.04 Å would not hold for S in galena, and the values obtained for Se and Te would be wrong, although they would still represent the correct relative sizes in comparison to S.

ARGENTITE

The similarity of the crystal forms of argentite and galena is apparently good evidence for considering them isomorphous. The cube, octahedron, and dodecahedron are commonly observed on both minerals. However, argentite crystals are frequently distorted. Distortion usually refers to an unequal development of faces belonging to the same form, without any change in the angular position of the faces. In the case of argentite, the interfacial angles are sometimes distorted. For example, the specimen referred to as number 2 occurred in well formed crystals, which at first glance appeared to be octahedrons. Measurement of the angles showed, however, that instead of the theoretical value of approximately 70° , they were actually about 63° . The significance of this will be discussed later.

Six specimens of Ag_2S were used, as follows: (1) a crystal from Saxony, which appeared to be a cube in combination with a trigonal

trisoctahedron; (2) the steep octahedral crystal already mentioned, from Mexico; (3) and (4) massive specimens from an unknown locality; (5) material artificially prepared by precipitation from solution; and (6) material artificially prepared by the direct union of the elements. All six samples gave identical diffraction patterns of an unexpected type.

It is well known that the interplanar spacings in a cubic crystal have a very simple relationship. If a_0 be the length of the side of the unit cube, or in other words, if $a_0 = d_{100}$, then the spacing for

any other plane hkl for any order n is equal to
$$\frac{a_0}{\sqrt{(nh)^2 + (nk)^2 + (nl)^2}}.$$

This means that no matter what the absolute size of a cubic struc-

ture, the spacings are always in the ratio of $\frac{a_0}{\sqrt{1}} : \frac{a_0}{\sqrt{2}} : \frac{a_0}{\sqrt{3}} : \frac{a_0}{\sqrt{4}}$, etc.

It is accordingly possible to calculate the spacings for all possible planes in terms of a_0 . In Table I, for instance, all planes with

spacings from $\frac{a_0}{\sqrt{1}}$ to $\frac{a_0}{\sqrt{24}}$ were listed. Not all of these gave reflec-

tions, however; but since there are no other possible planes with spacings within the above limits, there can be no other reflections than those which correspond to these planes. Any additional reflection would correspond to a plane with impossible spacings.

If the spacings calculated from an extended series $\frac{a_0}{\sqrt{1}} : \frac{a_0}{\sqrt{2}} \dots$

are plotted on a logarithm scale, then the differences due to the different values of a_0 disappear. Whatever the absolute value of a_0 , the relative spacings would be the same, and all cubic structures would be comparable. Such a plotting of the logarithms of the spacings might be referred to as a generalized cubic diffraction pattern. No matter how complex a cubic structure might be, it could not have lines in its diffraction pattern which did not correspond to this general pattern if they were plotted on a logarithm scale.

It was stated that the diffraction pattern from argentite was of an unexpected type. The spacings as determined from its pattern were plotted on the logarithm scale and there was no agreement with the generalized pattern. Not only do the lines occur in different positions, but their spacings are much closer together.

There are two possible explanations for this. As the interplanar spacings become smaller the lines of the pattern are much closer together. These lines correspond to planes of either high orders or of complex indices, and are usually secured from complex structures. The first explanation, then, would be that argentite has a complex cubic structure, and that its lines would match the generalized pattern in the region where the lines are very close together. Such a matching is difficult to detect because the error involved becomes as great as the distances between adjacent lines. This explanation, however, is not in accord with the available crystal structure data. Simple compounds appear to have simple structures, and there would seem to be no justification for assuming a simple compound like Ag_2S to have a complex structure. The second explanation is more reasonable: namely, that argentite is not cubic. Structures other than cubic are apt to have the lines in their patterns crowded close together. This is illustrated by comparing the cubic and orthorhombic systems. In the cubic, where the three axes are all equal, the planes 001, 010, and 100 are identical, as are also 110, 011, and 101; or 123, 132, 213, 231, 312, and 321; etc., while in the orthorhombic these would all be different, and would have different spacings. This fact makes the patterns of such crystals usually very complex, and the solution of their structures is difficult.

Doubt as to the true cubic character of argentite is suggested by the distorted angles observed on some crystals. Furthermore, Ag_2S occurs also as the mineral acanthite, classed by Dana³ as orthorhombic, but possibly merely distorted argentite. Several specimens of acanthite were available and all gave diffraction patterns identical to those from argentite, indicating that there is no difference in structure between the two minerals. The apparently authentic cubic forms on argentite can be accounted for by assuming that Ag_2S has a high temperature cubic modification, which is unstable at lower temperatures. A crystal formed as cubic would retain its general outward form on cooling, but would undergo molecular readjustment, becoming a pseudomorph of acanthite after the high temperature form. This is somewhat similar to the case of the mineral leucite, which is cubic above 500°C . Below this temperature there occurs a readjustment, involving the formation of a complex twinned structure, composed of orthorhombic individuals. The outward form is still apparently cubic, with only very slight changes in the interfacial angles.

In regard to argentite, the uninterpreted diffraction pattern is insufficient to prove it to be orthorhombic. However, it is identical with acanthite, and both are entirely different from galena. The two probably have structures similar to orthorhombic chalcocite, Cu_2S . It should also be emphasized that even a high temperature cubic form could not be structurally isomorphous with galena, because two Ag atoms could not be equivalent to one Pb atom.

HESSITE

A specimen of hessite from Transylvania was available for investigation. This gave a diffraction pattern very similar to argentite, indicating that this mineral, also, is not isomorphous with galena. This furnishes additional proof that Ag_2 is not equivalent to Pb in a crystal structure.

EUCAIRITE

There is no mineral corresponding to the composition Ag_2Se , so eucairite was used. The Ag and Cu selenides should be able to form mixed crystals, and it would be expected that $(\text{Ag}, \text{Cu})_2\text{Se}$ would have the same structure as Ag_2Se . The specimen available was not pure. The eucairite was intimately mixed with an unknown mineral, and both were embedded in calcite. The latter was removed by treatment with dilute acid, while the former was partially removed by hand sorting under a magnifying glass. The diffraction pattern secured may not be due entirely to eucairite, but none of the lines agreed with the generalized cubic pattern.* The introduction of the Cu atoms would change the crystallographic constants so that the pattern could not be expected to resemble that of argentite. While there is no direct proof of isomorphism with argentite, it is clearly established that eucairite is not isomorphous with galena.

NAUMANNITE

It was thought that the study of a compound such as this might throw some light on the relation of galena and argentite. If they are isomorphous, they ought to be able to form mixed crystals, with the Ag and the Pb in varying proportions. If they are not isomorphous, mixed crystals should not occur.

No specimen of naumannite was available, but the corresponding sulfide was prepared artificially. Two alloys of Pb and Ag were made, one with about 13 per cent and the other about 20 per cent

of Ag. These were finely divided, mixed with sulfur, and heated. The heat of the reaction drives off the excess sulfur not needed for combination.

The diffraction pattern from these two PbAg sulfides proved to be that of pure PbS, which was rather unexpected. It was expected that the pattern would either be that of a mixture of the two sulfides, or else correspond to a PbS structure with a different sized unit cell, because of the presence of the Ag atoms. Since the unit cell is of the same size, it must mean that there are no Ag atoms replacing Pb atoms in the structure.

There is a marked difference in the readiness with which lead and silver combine with sulfur. Molecular quantities of lead and sulfur unite rapidly with evolution of heat, while to form Ag₂S it is necessary to use excess sulfur and prolonged heating. It may be that the lead in the alloy combined with the sulfur, while the silver did not. In that case the silver would be mechanically held in the PbS structure. It would not be present as crystallized silver, and hence would not give the silver diffraction pattern.

This again supports the conclusion that PbS and Ag₂S are not isomorphous. The X-ray evidence in each case has indicated this fact. This does not establish the general conclusion that two monovalent atoms can never replace a single bivalent atom in a given structure, but it does prove it in this case, and further study of similar cases will probably show the same results.

THE PYRITE GROUP

This group consists of the following minerals:

Pyrite	FeS ₂
Hauerite	MnS ₂
Sperryite	PtAs ₂
Ullmannite	NiSbS
Gersdorffite	NiAsS
Cobaltite	CoAsS
Smaltite	CoAs ₂
Chloanthite	NiAs ₂

These minerals occur in good crystals, the pyritohedron, cube, and octahedron being commonly observed. Their compositions are entirely analogous, and the series has long been considered as a well established case of isomorphism. It is only recently that any question has been raised as to the validity of this isomorphism.

Cobaltite occurs in perfectly formed crystals, and has been found by both the Braggs⁴ and Mechling⁵ to have the pyrite structure, but Schneiderhöhn⁶ reports that it is not cubic at all. His examination of polished sections of the crystals by reflected polarized light revealed a structure made up of intimately twinned orthorhombic individuals. This, again, would seem to suggest a condition similar to the mineral leucite, which was referred to under the discussion of argentite as having high and low temperature modifications. If this be the true explanation, it would mean that the high temperature form was isomorphous with pyrite, rather than the ordinary or low temperature form. But, this does not explain the results secured by the Braggs and Mechling. It was thought that further investigation might settle this question.

PYRITE

The structure of pyrite has been worked out very thoroughly^{7,8}. Four molecules of FeS_2 are associated with each unit cell. The Fe atoms lie at the corners and face centers of the unit cube, the length of whose edge is 5.38 Å. This unit cube can be thought of as divided into eight smaller cubes by passing planes through the center—from top to bottom, from side to side, and from front to rear. The alternate corners of one of these cubes will be occupied by the Fe atoms, and any diagonal through the center will always run from a corner occupied by an Fe atom to a vacant one. A sulfur atom is situated in each cube and lies on the diagonal toward the vacant corner, at a distance from it of approximately one fifth of the length of the diagonal.

A powder photograph of pyrite was made, and the diffraction pattern secured was used as the standard by which to judge the other members of the group. The planes represented in the pattern are shown in Table III, together with their observed intensities of reflection.

HAUERITE

This mineral was not included in this investigation. Its structure has been determined⁹ and there is no question concerning its isomorphism with pyrite.

SPERRYLITE

The diffraction pattern from sperrylite is essentially the same as that from pyrite. There are differences in the relative intensities,

due to the difference in reflecting power of the Fe and S atoms, as compared with the Pt and As. The theoretical and observed intensities for the important planes are shown in Table III. For calculating the theoretical values it was assumed that the Pt and As atoms were both larger than the Fe and S in the same general proportion. Thus the As atoms should occupy the same relative positions on the diagonals of the small cubes as do the S atoms in pyrite. The observed intensities and those calculated on this basis agree fairly well, indicating that this assumption is approximately correct. The size of the unit cube of sperrylite was found to be 5.94 Å.

ULLMANNITE

Ullmannite is of interest because crystals have been observed which have lower symmetry than that of pyrite. The ordinary form is the cube, sometimes with pyritohedral striations. Miers¹⁰ reports the occurrence of tetrahedral forms on crystals from Carinthia. The combination of tetrahedral and pyritohedral symmetry means that the crystals should be referred to the lowest symmetry class of the cubic system. The explanation has been given that this lower symmetry is due to the substitution of an Sb atom for one of the two S atoms. In pyrite the sulfur atoms are symmetrically placed with respect to three planes at right angles to each other. Since the Sb atom is not equivalent to the S in size, its substitution in alternate positions occupied by S would destroy this symmetry. No statement of an actual proof for this kind of a structure is on record, nor are there any data concerning the size of the unit cell.

The diffraction pattern is fairly similar to that of pyrite, and indicates that the structure is the same. The Sb atoms must occupy alternate positions with the S, for no other arrangement would be possible according to the theory of space groups.

Nickel has practically the same reflecting power as iron, but the presence of the antimony should make an appreciable difference in the relative intensities of reflection from pyrite and ullmannite. This is shown in Table III, where the observed intensities are given. In pyrite the planes 311, 211, and 210 have the intensities 1, 5, and 4 respectively, whereas in ullmannite these same planes are rated as 1.5, 2, and 1.

By assuming that the Sb atoms occupy the same relative position on the diagonals of the small cubes as do the S atoms in pyrite, the

calculated values do not agree closely with the observed intensities. For example, the reflection from the plane 111 was plainly visible, although not very intense, but according to the calculated value it should have been too weak to appear at all. Apparently, the positions have been slightly changed with reference to pyrite. The whole structure is, of course, on a larger scale because of the introduction of the larger Sb atoms. It is evident from a study of a three dimensional model of the structure that the Sb atoms would lie a little closer, and the S atoms a little farther from the vacant corners of the small cubes than do the S atoms in pyrite. By making such a change arbitrarily, the calculated results given in Table III were secured, and it will be seen that the agreement is fair.

The reflection obtained from the 100(2) plane gave a value of 5.91 Å for the length of the side of the unit cube.

GERSDORFFITE

The first specimen examined was from Austria and gave a diffraction pattern identical to those which were obtained from smaltite, indicating that it was NiAs_2 rather than NiAsS . A second specimen, from Germany, proved to be gersdorffite. Its diffraction pattern is quite analagous to that of ullmannite, as would be expected. The side of the unit cube was found to be 5.68 Å. It should be pointed out that such dimensions as these refer only to the specimen examined. The size of the unit cell may vary greatly because of the extensive replacements which occur in the sulfide minerals. Gersdorffite, for example, may contain from 2 to 6 per cent of iron, small amounts of cobalt, and sometimes antimony. To obtain exact measurements of the unit cell, artificially prepared pure material would have to be used.

COBALTITE

The conflicting evidence in regard to cobaltite has already been stated. The diffraction pattern secured in this investigation was a cubic one, and gave a value for the side of the unit cell of 5.58 Å. This confirms the results obtained by the Braggs and by Mechling. As far as is known, none of the crystals used for X-ray analysis were examined by reflected light. It would be easy to conclude, therefore, that these are all cubic, while those examined by Schneiderhöhn are orthorhombic. This scarcely seems possible, for Schneiderhöhn found that without exception all crystals examined

were orthorhombic. On the other hand, crystals from widely different localities were used for X-ray analysis, and all were uniformly cubic. It would seem necessary to conclude that either the X-ray data are correct, and the observations of Schneiderhöhn wrong, or that his observations are correct, and the X-ray data wrong.

The method of examining polished sections of crystals by reflected polarized light is a sound one, and there seems to be no ground for doubting the results. On the other hand, judging from the large amount of consistent X-ray data obtained from all types of compounds, it would seem unwarranted to conclude that apparently authentic data can be secured which are not in accord with the structure producing them. If both results are correct, there must be some manner of reconciling them. Two possibilities suggest themselves. The first is concerned with the relative sensibility of the X-ray methods, and the second with the surface effects which may be produced by grinding and polishing mineral sections.

The first possibility can be explained as follows: chalcopyrite, CuFeS_2 , crystallizes in the tetragonal system. Its axial ratio is 1:0.985, which is very nearly 1:1. Its diffraction pattern is, to all appearances, a cubic one, showing that X-rays, in the powder method at least, cannot distinguish between a cubic crystal and a tetragonal crystal with a value for the c axis so near to unity. It might be that the cobaltite structure is orthorhombic, but so nearly cubic that the X-ray data appear to be cubic.

Indirect evidence on this point can be obtained from pyrite and marcasite, the cubic and orthorhombic forms of FeS_2 , respectively. Their diffraction patterns, although similar in some respects, show distinct differences, and that of marcasite could not be interpreted as belonging to a crystal isomorphous with pyrite. There is no orthorhombic mineral with the exact composition CoAsS . However, glaucodot is orthorhombic and differs from cobaltite in composition only in the presence of some iron, its composition being $(\text{Co,Fe})\text{AsS}$. It gives an entirely different pattern than does cobaltite. It is logical to conclude, therefore, that there is sufficient difference between cubic and orthorhombic CoAsS to distinguish their diffraction patterns, and that cobaltite, if really twinned orthorhombic, ought not to give a cubic pattern.

It might be well to state at this time that there is no possibility of cobaltite simulating a cubic structure by means of twinning. Twinning does sometimes result in "mimicry," as in the case of orthorhombic aragonite, which appears to be hexagonal, but this mimicry is in outward form only. The structure of each of the various individuals making up the whole is unchanged. A Laue photograph through a section of a twinned crystal might be affected, but in the powder method there would be no effect unless the twinning were sub-microscopic, in which case it could not be detected by optical methods.

The second possible method of reconciling the conflicting evidence is based on the assumption that cobaltite is metastable at ordinary temperatures. It is a well known fact that the grinding and polishing of metallographic sections may bring about decided changes in the surface layers of atoms. Alling¹¹ reports that the process of grinding brings about the change from the metastable orthoclase to microcline, with the development of the characteristic microcline twinning. In order to obtain results by the use of reflected polarized light a very high degree of polishing is necessary. It might be that this process brings about a superficially twinned orthorhombic structure, while the interior remains unchanged. The observations on these sections are not made by transmitted light. A change in a few atomic layers would be sufficient to be detected by optical methods, while no effect at all would be observed on the X-ray photograph.

In a transparent substance it would be easy to determine whether or not such a change was limited to the surface, by the use of ordinary petrographic methods. In opaque substances, it should be equally easy to determine if a structural change had occurred throughout the crystal, by the use of X-rays. The evidence actually secured indicates that such a change has not taken place. There seems to be no way in which evidence could be secured as to the surface structure by X-ray methods, for it would be impossible to obtain these surface layers, only a few atoms deep, separate from the remaining unchanged material.

It is not possible to prove at present if this second possibility is correct, or whether still another explanation might be found. The whole question of the dimorphous sulfide minerals is one deserving further study.

SMALTITE AND CHLOANTHITE

These two minerals have the compositions CoAs_2 and NiAs_2 , respectively. The exact compositions represent the end members of a series of mixed crystals and rarely occur. The names smaltite and chloanthite are given to the various members of the series, depending upon which element predominates. There is so little difference between the Ni and Co atoms in size or in reflecting power that the diffraction patterns of the pure compounds should be very similar, and no difference at all should be observed when both Co and Ni are present in considerable amounts.

This was found to be true. Samples prepared from specimens from Germany, which qualitative tests showed to contain both Co and Ni, gave indistinguishable patterns. Specimens labelled "gersdorffite" and "skutterudite" also gave patterns of the same type, proving that they were actually either smaltite or chloanthite. In all, then, diffraction patterns were obtained from four samples.

These patterns are of a very puzzling nature. Except for two lines, they agree perfectly with a cubic arrangement. Calculations based on the density, the weight of a molecule, and the assumption that the unit cell contains four molecules, as does pyrite, give the length for the side of the unit cube of 5.96 \AA , which checks closely with the value determined from the pattern.

However, the intensities of the reflections actually observed do not agree with those calculated for the pyrite structure. The reflection from plane 210 is strongest, while the calculated value is fourth, and that from 100(2) is absent, while for the pyrite structure it is quite strong, being rated second. These two variations do not present any special difficulties, for the former can be accounted for by the increase in reflecting power of the As as compared to the S atom, and the latter by assuming a slight change in the relative position of the As atoms. In pyrite the S atoms lie on the diagonals of the small cubes toward the vacant corners. If the occupied corners are considered as the origin, the co-ordinates of an S atom would be uuu , where u equals $.338a_0$. (a_0 is the length of the edge of the unit cube). It is evident from a study of a three dimensional model that if larger As atoms be substituted for the smaller S, while Ni or Co are practically the same as Fe, the value of u would have to be less. In other words, the As atoms would not be so

relatively close to the vacant corners. By assuming u to have a value of about .350 instead of .388, the reflection from plane 100(2) disappears.

Other reflections have intensities that cannot thus be reconciled, however. The reflection from plane 211 is missing. If u were about .275, this could be expected, but if it is .350 as required by the plane 100(2), a medium strong reflection should occur. The reflection from plane 100(3) is present, although not intense, and that from 310 is very strong, but neither of these should be present for any values of u whatever in this type of structure. The reflection from 311 is weak, whereas it should be strong. In pyrite, this 311 reflection is the most intense, and no value of u can be assumed which will greatly reduce it.

The diffraction pattern presents two difficulties, then. Two lines do not fit in with a cubic pattern, and some of those that do fit do not have the intensities expected from the pyrite type of structure. The two lines are of such intensity that they cannot be ignored as being due to a trace of impurity. By assigning more complex indices to the planes, the pattern can be made to agree fairly well with a cubic arrangement, with the side of the unit cube 8.28 Å. But, a cell of this size would have to contain ten and a fraction molecules of either smaltite or chloanthite. The fraction might be due to a slight error in the density determination, but neither ten nor eleven molecules could be arranged in a cube with cubic symmetry.

It may be that we are not dealing with a homogeneous substance, and that the peculiar pattern is due to a composite effect. Extra lines in a diffraction pattern may be due to impurities. If the impurity is in solid solution the size of the unit cell might be changed but no new lines would appear in the pattern. If it is merely mechanically mixed with the substance, then each would give a pattern, the one superposed on the other. If it were present in only a small amount, only its most intense lines would appear.

Volkhardt¹² reports that when smaltite is treated with acid, a portion dissolves, leaving a residue with a higher percentage of arsenic—probably CoAs_3 . Baumhauer¹³ reports a zonal arrangement in smaltite crystals. Beutell¹⁴ states that smaltite crystals examined by him consisted of an outer zone of CoAs_2 , with CoAs_3 and Co_2As_3 on the inside. (In this same reference, Beutell says that skutterudite, CoAs_3 , is probably not cubic, but occurs as a pseudomorph after smaltite). This zonal structure seemed to offer an explanation

for the extra lines in the smaltite pattern. If they corresponded to the chief lines of the skutterudite pattern, the whole question would be solved.

It has been impossible to secure a single crystal of skutterudite. Extremely small crystals were picked out from a specimen labelled skutterudite, but they gave the CoAs_2 pattern, indicating that they were smaltite. Material consisting of an intimate mixture of skutterudite and smaltite was treated with sulfuric acid and KClO_3 , according to the method of Parsons,¹⁵ and a diffraction pattern secured from the residue, supposed to be CoAs_3 . If this residue is skutterudite, it is quite certain that Beutell was right, and that it is not cubic, for the pattern was very complex. Moreover, there were no lines in positions which would account for the irregular lines from smaltite and chloanthite. . . . If this really is the skutterudite pattern, it is eliminated as a possible cause of the extra lines.

Attempts to prepare NiAs_2 and CoAs_2 artificially have failed so far. If this can be done, it will be possible to determine if the unusual pattern was due to material other than the two diarsenides. Until this is done, it is not likely that an exact determination of their structures can be made, and their isomorphism with pyrite cannot be proved from the structural standpoint.

TABLE III. OBSERVED AND CALCULATED INTENSITIES OF REFLECTION

Plane	Pyrite	Sperrylite		Ullmannite	
	Observ.	Observ.	Calc.	Observ.	Calc.
111	5	x	550	x	12
100(2)	2	2	970	3	227
210	4	3	667	1	590
211	5	4	310	2	320
110(2)	3	2	870	4	119
311	1	1	1434	1.5	325

Explanation of table.—This table gives the observed values of the intensities of reflection from the most important planes of pyrite, and the observed and calculated values for the corresponding planes of sperrylite and ullmannite. For the observed values, 1 represents the most intense line. For the calculated values, the intensities are proportional to the number given. These numbers represent arbitrary units, and cannot be used in comparing the same planes from different minerals. The relative differences in the intensities for planes 311, 211, and 210 for pyrite and ullmannite is very apparent. The letter "x" indicates that the line was so obscured by the general blackening on the film that its comparative intensity could not be determined.

CINNABAR GROUP

The two minerals cinnabar (HgS) and covellite (CuS) have been considered as forming an isomorphous group. Their compositions are analagous, and both crystallize in the hexagonal system. Groth¹⁶ and Dana¹⁷ refer cinnabar to the trigonal trapezohedral class, with an axial ratio of 1:1.1453. They assign to covellite a ratio of 1:1.1466, but express doubt as to the class of symmetry to which it belongs. In view of this uncertainty, it was thought that X-ray data might be able to determine whether covellite had the same structure as cinnabar or not. If it did, its symmetry would be clearly established.

CINNABAR

There is a large difference between the reflecting power of the Hg and the S atoms, and it is to be expected that the diffraction pattern of cinnabar would be determined chiefly by the position of the Hg atoms. The pattern indicates a simple rhombohedral arrangement for these Hg atoms, with the actual lengths of the a and c axes 4.15 Å and 9.51 Å, respectively. This unit rhombohedron has an axial ratio of 1:2.29, which gives c a value just twice that which has been assigned to the crystals. In Table IV the spacings for the various planes which recorded reflections on the film are compared with the calculated values for a rhombohedron of the dimensions given above.

The customary calculations, involving the density of cinnabar, the volume of the unit cell, and the weight of one molecule of HgS, indicate that a single molecule is associated with this unit cell. If cinnabar possesses trigonal trapezohedral symmetry, then there is only one way of placing the two atoms, Hg and S, in the cell. The Hg atom would have the co-ordinates 000, and the S atom $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. In other words, there would be a Hg atom at each corner of the rhombohedron, and a S atom in the center. Each corner Hg atom would be shared in common by eight adjacent rhombohedrons, so that only one eighth of each atom would belong to an individual rhombohedron; but there are eight corners, so there would be a total of eight eighths belonging to each unit cell. The S atom at the center, would, of course, furnish one atom for every cell.

At first sight the steep rhombohedral character of the unit cell seems to represent a less simple structure than that of the similar compounds PbS (galena), which is face centered cubic. As a matter of fact, its structure is very much like that of galena. There is no

special significance to this similarity, except that it shows that there is no great difference in structure involved in this change to lower symmetry, and the type of bond between the atoms must be quite similar.

The rhombohedron of cinnabar could be thought of as a greatly distorted cube, but this would involve a change in the axial ratio (regarding the cube as a special rhombohedron with an angle of 90°) from 1:1.22 to 1:2.29. (Figure 1a). This would mean that there was a considerable difference in the interatomic forces of the two compounds.

A more simple relationship between galena and cinnabar can be found. The points of a face centered cube can be connected so as to form a rhombohedron. (Figure 1b). This has an axial ratio of 1:2.45. A slight compression along the c axis would change this to a rhombohedron with the ratio found for cinnabar: namely, 1:2.29. The relative change involved is shown in Figure 1c.

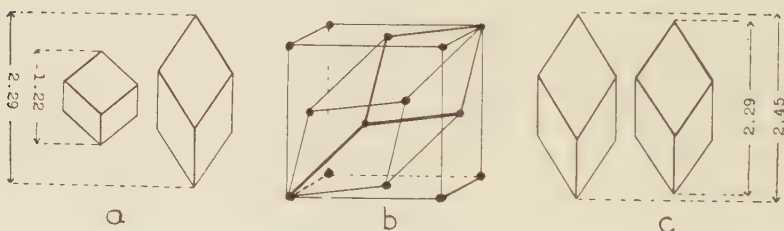


FIGURE 1

In this change the face-centered-cube positions of the Pb atoms in the galena structure become the rhombohedron-corner positions of the Hg in cinnabar. The S atom at the center of the galena cube would still be at the center of the rhombohedron. It is not easy to visualize the change from the old positions of the S at the middle of the cube edges in galena to the new position in the rhombohedron. However, they would fall into their proper places at the centers of adjacent rhombohedrons, and every position of the galena cube would have its equivalent position in the cinnabar structure. There is, therefore, a very close relation between the two structures. The two minerals cannot be considered isomorphous, because they are essentially different in their crystallographic properties, and yet a slight deformation will derive either structure from the other.

Cinnabar is optically active: that is, it rotates the plane of polarized light. This property is usually attributed to a spiral arrangement of the atoms which the rhombohedral structure found for cinnabar does not possess. It may be here, again, that we have a case in which a very slight deviation from the rhombohedral arrangement is not detected by the X-ray analysis, and yet is sufficient to make a marked difference in the optical properties.

COVELLITE

Because of the doubt as to the proper symmetry class to which covellite should be assigned, it was thought that a determination of its structure would show whether or not the symmetry was lower than that of cinnabar. The diffraction pattern was different than was obtained for cinnabar. This in itself is of no significance. In the cubic system all crystals can be compared if their spacings, as recorded on the diffraction patterns, are plotted logarithmically. In all the other systems crystals are not thus comparable unless they have the same axial ratios, for a very slight change in the ratio may make a marked difference in the position, or even in the number, of lines in the pattern. Covellite has an axial ratio similar to cinnabar, but there could very well be some difference in the pattern. The pattern secured, however, did not agree with a simple rhombohedral arrangement of any axial ratio whatsoever.

Attempts were made to secure Laue photographs to establish the symmetry and to give additional information as to the structure. Covellite has perfect basal cleavage, and the photographs were taken with the X-ray beam perpendicular to the cleavage plane. Instead of the usual pattern of spots, only streaks radiating from the center were secured. These are usually attributed to deformation of the crystal, so it may be that the rather soft plates were bent by handling. Even with careful manipulation, however, no better results were secured in repeated attempts.

The actual structure of covellite cannot be deduced from the available evidence, but it does seem clearly established that it is not isomorphous with cinnabar, and probably does have a different symmetry.

TABLE IV. OBSERVED AND CALCULATED SPACINGS FOR CINNABAR

Plane	Observed spacings	Calculated spacings
10 $\bar{1}$ 1	3.36Å	3.36Å
0001	3.17	—
01 $\bar{1}$ 2	2.87	2.865
11 $\bar{2}$ 0	2.08	2.074
10 $\bar{1}$ 4	1.98	1.980
02 $\bar{2}$ 1	1.764	1.764
11 $\bar{2}$ 3	1.73	1.735
10 $\bar{1}$ 1(2)	1.680	1.680
0001(2)	1.580	1.585
10 $\bar{1}$ 2(2)	1.440	1.432
21 $\bar{3}$ 1	1.340	1.344
12 $\bar{3}$ 2 2025)	1.312	1.305

SUMMARY

GALENA GROUP—Clausthalite and altaite have structures similar to galena, but with larger unit cells, while the other members of the group do not have the galena structure, and hence are not isomorphous with galena. They are probably orthorhombic. The existence of argentite and acanthite as two separate minerals is definitely disproven. The cubic form of argentite is explained as a pseudomorph after a high temperature form of Ag_2S .

PYRITE GROUP—Sperrylite has the same structure as pyrite, as does also ullmannite. The lower symmetry of the crystals of the latter is accounted for by the substitution of larger Sb atoms for half of the S atoms. Gersdorffite is very similar to ullmannite and has the same symmetry, although no crystals have been observed which showed this. The X-ray data indicate that cobaltite likewise has the pyrite structure, with the same symmetry as ullmannite. A possible explanation is given to account for the optical data which apparently contradict the X-ray evidence concerning the crystal form of cobaltite. Smaltite and chloanthite should be isomorphous with pyrite, but the X-ray data are decidedly unsatisfactory, and no explanation could be found for the diffraction patterns, although it may be that the crystals were not homogeneous.

CINNABAR GROUP—A simple rhombohedral structure is deduced for cinnabar from the X-ray data. The unit rhombohedron has an axial ratio twice that usually given to the crystals, and contains one molecule of HgS . Although the structure of covellite was not

determined, the evidence showed that it is unlike that of cinnabar, and that they are not isomorphous.

CONCLUSIONS

Isomorphism is essentially a means of classification, and its validity depends upon the extent to which it is based on fundamental rather than superficial facts. The ordinary conception of isomorphism antedates any knowledge of actual crystal structure. In an attempt to get at more fundamental relationships than were evident from the crystal form, there were introduced such ideas as equivalent parameters¹⁸ and topical axes for molecular distance ratios¹⁹; but still more fundamental than these is the structure itself, of which all these others are merely expressions. Since there is now a means of determining the structures, it is possible to base isomorphism directly upon them.

Ordinarily the crystal form can be regarded as fundamental, but apparently there are cases where this cannot be done. The crystals of argentite are either pseudo-cubic, or, if the structure be assumed to be complex cubic and not orthorhombic, their resemblance to the crystals of galena is merely a coincidence. This likewise applies to hessite, eucairite, and naumannite. In the pyrite group, the lower symmetry of ullmannite is not due to any fundamental difference in structure. It still has the pyrite structure, and should be considered isomorphous with it.

If structure is to be the criterion of isomorphism, we should no longer have isomorphous groups in which the members have a different number of atoms. An exception to this might have to be made to cover the substitution of a group such as NH_4 for a single monovalent atom. The indications are that this group functions as a crystallographic entity as well as a chemical entity²⁰ and can occupy a position in a structure analagous to that occupied by a single atom; but in no way could two Ag atoms in Ag_2S occupy a position corresponding to one Pb atom in PbS , without violating the principles of space group theory.

Not only can the structure be used instead of the crystal form in determining isomorphism, but it also has a direct bearing on the analogy in chemical compositions. Apparently similar compounds may have the same number of atoms with the same valences, and yet have different structures, as HgS and CuS . This means that valence alone is not sufficient to determine the analogy in composi-

tion. Hg and Cu do not occur in the same family of the periodic table, and the atoms themselves are not of analagous types, so there is no reason to expect the two compounds to have similar structures. On the other hand there are cases of isomorphous groups with elements from different families. It would seem best, then, to make the criterion of analogy the similarity of interatomic forces, which, in turn, means similarity of crystal structures.

In the majority of cases the old definition of isomorphism will suffice, but the analogy in chemical composition must be understood as applying only to such compounds as have analagous structures, as well as similar chemical natures. Moreover, it must be remembered that while the crystal form ordinarily is an accurate expression of the structure, it may be at variance with it. In such cases the criterion to be used must be the more fundamental of the two, the crystal structure.

REFERENCES

- ¹ W. H. and W. L. Bragg: X-RAYS AND CRYSTAL STRUCTURE (1st ed.) p. 173 (1915).
- ² R. W. G. Wyckoff: THE STRUCTURE OF CRYSTALS, p. 107, (1924).
- ³ E. S. Dana: SYSTEM OF MINERALOGY, (6th ed.) p. 55, (1914).
- ⁴ W. H. and W. L. Bragg: X-RAYS AND CRYSTAL STRUCTURE (4th ed.) p. 144 (1924).
- ⁵ Mechling: *Aband. Math. Phys. Akad. Wiss. Leipzig*, 37-51 (1921).
- ⁶ Schneiderhöhn: ANLEITUNG ZUR MIKROSKOPISCHEN BESTIMMUNG VON ERZEN IN AUFFALLENDEN LICHT. Berlin (1922).
Abstr. *Econ. Geol.*, **18**, 604 (1923).
- ⁷ W. H. and W. L. BRAGG: X-RAYS AND CRYSTAL STRUCTURE, (4th ed.) p. 115-121 (1924).
- ⁸ Ewald: *Ann. d. Physik*, **44**, 1183, (1914).
- ⁹ Ewald: *Ann. d. Physik*, **44**, 1183, (1914).
- ¹⁰ H. A. Miers: MINERALOGY, p. 332 (1902).
- ¹¹ Alling: *Jour. Geol.*, **29**, 194-294 (1921).
- ¹² Volkhartdt. *Z. Krist.*, **14**, 407 (1888).
- ¹³ Baumhauer. *Z. Krist.*, **12**, 15 (1886).
- ¹⁴ Beutell: *Centr. Min. Geol.*, 206-221 (1916).
- ¹⁵ Parsons: Contributions to Canadian Mineralogy, p. 9, (1924).
- ¹⁶ Groth. Tabellarische Übersicht der Mineralien p. 28, (1898).
- ¹⁷ E. S. Dana: SYSTEM OF MINERALOGY. (6th ed.) p. 66 (1914).
- ¹⁸ Barlow and Pope: *Chem. Soc. Trans.*, **89**, 1675 (1906).
- ¹⁹ Muthmann. *Z. Krist.*, **22**, 497 (1894); Tutton: *Chem. Soc. Trans.*, **65**, 628 (1894).
- ²⁰ R. W. G. Wyckoff: THE STRUCTURE OF CRYSTALS, p. 320, 1924.

THE THERMO-OPTICAL PROPERTIES OF HEULANDITE*

CHESTER B. SLAWSON, *University of Michigan*

Abstract

Heulandite shows two characteristic changes in its optical properties with rising temperature, a rotation of the optic plane and a variation in the size of the optic angle. If these changes in the optical properties are plotted against the temperature, the curves fall into two distinct sections. The first portion, 25°-190° C, is characterized by a gradual and progressive rotation of the optic plane and by a decrease in the size of the optic angle. The second portion shows a rapid rotation of the optic plane and an increase in the optic angle. This change in the character of the curves is correlated with the development of the three molecule hydrate. The uniaxial point, which has been reported previously, is only apparent and is due to the rapid rotation of the optic plane when the optic angle is very small.

A similar change in the optical properties may be observed by dehydrating the crystals at room temperature with concentrated sulphuric acid. Laue diagrams taken at various temperatures show a gradual breaking down of the crystal structure if the crystals are dehydrated at a temperature above 190° C. This breaking down of the structure cannot be observed immediately after dehydration, as the original structure persists in a metastable condition, but the change is very pronounced a few months after dehydration.

INTRODUCTION

Unlike most hydrated salts, the zeolites do not break down and lose their crystalline form when dehydrated. As the dehydration progresses the crystals gradually become cloudy and finally opaque, but they regain their original transparency by absorbing moisture from the air. A crystal which has been dehydrated until it is opaque will likewise become transparent if it is allowed to absorb oil, alcohol, or some other organic liquid.

These peculiar properties of the zeolites were observed by early investigators and were attributed to a sponge-like structure of the crystals. Johnsen¹ has explained these phenomena by a phase of "solid solution," while Doelter² has considered this action to be due to "colloidal adsorption" of the water by the crystal.

In 1915 A. Beutell and K. Blaschke³ attempted to correlate the behavior of the zeolites with that of the characteristic hydrated salts. For desmine, a zeolite dimorphous with heulandite, they found

* From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, June, 1925.

¹ Die Anomalen Mischkristalle: *Neues Jahrb. f. Min.*, **2**, 93-138 (1903).

² *Phys. Chem. Mineralogie*, p. 179, (1905).

³ Das Wasser im Desmin ist chemisch gebunden: *Centr. f. Min.*, 4-11, (1915).

that the dehydration curve was discontinuous. The curve, which was constructed by plotting water content against the temperature, was step like, showing no loss of water through certain temperature intervals. In 1919 G. Stoklossa⁴ carried the same relationship over into the rest of the zeolites. His methods were similar, consisting of the determination of the water driven off with increasing temperature, and indicated significant "Haltepunkte" whenever the water was present in molecular ratios. At most of these points he examined cleavage fragments under the microscope and noted the variations in the optical properties as further evidence of the existence of definite hydrates. The uniaxial point of heulandite, which Rinne⁵ had previously reported as existing between 80°-100° C. he attributed to the "Kompensationerscheinung" between the 9 molecule hydrate and the 10 molecule hydrate (doubled formula) whose transition point he had found to be at 80° C.

Weigel's⁶ work which was published in the same year gave results of a decidedly different character. He found that the water of heulandite was driven off gradually and not in molecular ratios. The curve of dehydration was reversible up to 180° C. when a definite breaking point was reached which indicated the formation of a new hydrate. Scheuman⁷ gave similar results but established 186° C. as the temperature at which the three molecule hydrate was formed.

In 1921 Beutell⁸ brought forth some new experimental data in a series of two articles upon "Die Wasserbindung im Heulandit" to verify his previous work. Weigel⁹ published two articles upon "Zur Frage der Wasserbindung in den Zeolithen" in reply to Beutell. He introduced no new experimental data but referred to the confirming results of Scheuman which had appeared in the meantime.

Unfortunately, there is very little data available upon the vapor pressures of the hydrated silicates. Tammann¹⁰ has determined the

⁴ Ueber die Natur des Wassers in dem Zeolithen: *Neues Jahrb. f. Min.*, 1-64 (1919).

⁵ Ueber Faujasit und Heulandit: *Neues Jahrb. f. Min.*, 2, 17-38 (1887).

⁶ Sitz. Ber. Ges. z. Beforderung d. ges. Naturw. Marburg, 48-63, (1919).

⁷ Ueber die Wasser die Heulandit: *Verh. d. Sächs. Akad. Wiss., Leipzig, Math-Phys. Kl.*, 1-113 (1921).

⁸ *Centr. f. Min.*, 694-702, 721-734 (1921).

⁹ *Centr. f. Min.*, 164-178, 201-208 (1922).

¹⁰ Ueber die Dampfspannung von Kristallierten Hydraten: *Z. Phys. Chem.*, 27, 323-336 (1896).

vapor pressures of a number of the zeolites, including thomsonite, natrolite, phillipsite, harmotome, and chabazite, by allowing the crystals to stand over known concentrations of sulphuric acid. He plotted the vapor pressures against the loss of water and obtained a continuous curve. Upon the basis of Tamman's work, Findlay¹¹ uses the zeolites as typical examples of solid solution somewhat similar to the absorption of hydrogen by palladium.

The variations in the optical properties of heulandite with an increase in temperature has been noted by DesCloizeaux,¹² Mallard¹³ Klein,¹⁴ Rinne,¹⁵ Stoklossa,¹⁶ and Weigel.¹⁷ In all of these cases the observations were made under the microscope, upon sections which had been previously heated, and gave conflicting results, because no attempt was made to observe the changes continuously under well controlled temperatures. These changes have been generally ascribed to the loss of water.

The purpose of this investigation is to measure the variations in the optical properties of heulandite which accompany an increase in temperature and to determine what relationship these changes bear to the dehydration of the mineral.

EXPERIMENTAL DATA

The optical properties of heulandite were determined upon the large well developed crystals found in the amygdaloidal cavities of the basaltic rocks at Berufiord, Iceland. These crystals varied in size from 5 to 15 mm. wide, 10 to 30 mm. long, and 5 to 15 mm. thick. The excellent cleavage parallel to (010) gave nearly perfect sections 1 to $1\frac{1}{2}$ mm. thick. The indices of refraction were determined with the Abbe refractometer upon a polished pinacoidal cleavage section at 25° C. and gave for sodium light the following values: $\alpha = 1.4991$, $\beta = 1.5008$, $\gamma = 1.5052$.

These values give a calculated angle of $73^{\circ} 20'$ for the apparent angle (2E) of the optic axes in air. The measured value for the same section at 25° C. was $74^{\circ} 38'$. The angle of the optic axes

¹¹ THE PHASE RULE, p. 140, (1923).

¹² MANUEL DE MINERALOGIE, p. 426, (1862).

¹³ De l'action de la Chaleur sur la Heulandite: *Bull. Min. Fr.*, **5**, 255-260, (1882).

¹⁴ Beiträge zur Kenntniss der optischer Aenderung in Krystallen unter dem Einflusse der Erwärmung: *Z. Kryst.*, **9**, 38-72 (1884).

¹⁵ Ueber Faujasit und Heulandit: *Neues Jahrb. f. Min.*, **2**, 17-38 (1887).

¹⁶ Ueber die Natur. des Wassers in dem Zeolithen: *Neues Jahrb. f. Min.*, 1-64 (1919).

¹⁷ *Sitz. Ber. Ges. z. Beforderung d. ges. Naturw. Marburg*, 48-63 (1919).

varied slightly from crystal to crystal but all measured values fell between the limits of 68° and 76° . The orientation of the optical directions at 25° C. is shown in Figure 1. The acute bisectrix is parallel to the b -axis and the crystal is positive.

The analysis was made upon the same Berufjord, Iceland, crystals that were used for the determination of the optical properties. Column 1 shows the composition as determined by analyses at 25° C. and column 2 gives the theoretical composition calculated from the formula $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$.

	1.	2.
SiO_2	58.55	57.66
Al_2O_3	17.64	17.86
CaO	5.82	8.91
SrO	0.59	—
Na_2O	1.25	—
K_2O	0.81	—
H_2O	15.88	15.57
	<u>100.54</u>	<u>100.00</u>

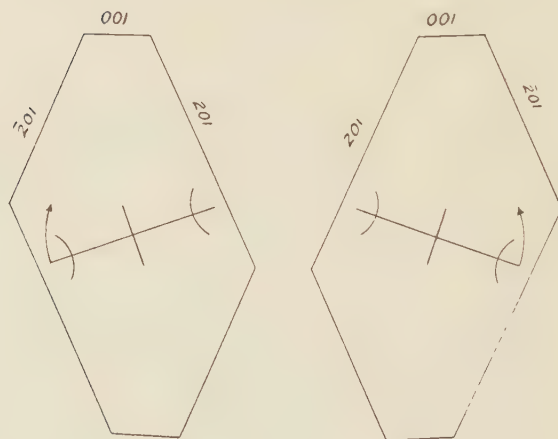


FIG. 1

OPTICAL ORIENTATION OF HEULANDITE

Heulandite has a very low double refraction, $\gamma - a = 0.0061$ and $\beta - a = 0.0017$. An interference figure is not dependent upon the absolute magnitude of the double refraction but rather upon the relative value of the double refraction in different directions through the crystal. Hence, a small change in the magnitude of the indices

of refraction will produce a relatively large change in the interference pattern. This is more pronounced in crystals of low double refraction than in those with high double refraction. In any consideration of the optical changes in heulandite it is well to bear this fact in mind, because large variations in the size of the optic angle and in the position of the optic plane may be brought about by slight distortions in the structure of the crystal.

The size of the optic angle and the position of the optic plane of heulandite are dependent upon the temperature and the state of hydration of the crystal. With an increase in temperature the optic plane rotates counter-clockwise upon (010) and clockwise upon (0 $\bar{1}$ 0). The acute bisectrix remains perpendicular to these faces.

DETERMINATION OF THE OPTICAL ROTATION

The rotation of the optic plane with an increase in temperature was measured directly from the interference figures by using the Groth axial angle apparatus. To measure the rotation of the optic plane with the crystal mounted in an oil bath it is necessary to rotate the horizontal cross hair to follow the movement of the optic plane while the crystal remains stationary. The analyzing tube was fitted with a graduated circle reading to 5' which measured this rotation. The polarizing and analyzing nicols were then connected so that they would rotate simultaneously and independently of the cross hairs.

The crystals were studied in an electrically heated oil bath, which was mounted between the condenser and the objective. This bath was constructed of brass and was 22 cm. long, 5 cm. deep, and 2½ cm. wide. The bath was enclosed in an asbestos fiber board case to prevent the radiation of heat. The thermometers were calibrated with a standard thermometer inserted in the same position as the crystal section and were corrected for stem emergence.

DETERMINATION OF THE OPTIC ANGLE

The angle of the optic axes for any crystal may be determined directly by mounting the crystal horizontally and rotating it so that the optic axes will come successively to the cross hairs. This will give the angle of the optic axes at room temperature but it will not give the true angle if the plane of the optic axes has rotated from the horizontal. A close approximation of the sine of H (2H being the observed angle of the optic axes in oil) may be made by

dividing the sine of half the angle of rotation, which is necessary to bring the optic axes successively to the cross hairs, by the cosine of the angle of rotation of the optic plane. Because of the inaccuracies of this method, the angle was calculated from the photographs of the interference figures.

Mallard¹⁸ has shown that for any given lens system the distance from any point in the interference figure (as formed in the rear focal plane of the objective), to the center of the field is proportional to the sine of the angle formed by the axis of the microscope and a ray of light striking at that point. If the acute bisectrix is parallel to the axis of the microscope (emerges in the center of the field) then the distance from the center of the field to one of the optic axes is proportional to the sine of half the angle of the optic axes. From a section whose optic angle is known, a constant K (Mallard Constant) for the lens system may be computed from the formula

$$K = \frac{D}{\sin H} . \quad \text{By applying this constant K, the value of an un-}$$

known optic angle may be computed by measuring its distance from the center of the field. This is the principle upon which the engraved scale which is inserted in the rear focal plane of the objective of the Axial Angle Apparatus is made. Becke¹⁹ has developed a graphic method based upon the same principle.

By carrying this principle still further it may be used in calculating optic angles from photographs. The crystal is mounted with the optic plane horizontal and the optic angle measured by rotating the crystal. The interference figure is then centered in the field and photographed. From the known optic angle and the distance of the optic axes from the center of the photograph, a constant K may be calculated for the lens systems of the objective and of the camera, and for the distance of the photographic plate from the crystal. Then, by applying this constant to photographs taken with the same lens systems similarly focused, the unknown optic angles may be calculated.

The calculation of the optic angles from the photographs of the interference figures is very accurate because the distances are measured upon the photographic images which are enlarged four

¹⁸ *Bull. Soc. Min. Fr.*, 5, 77-87 (1882); also F. E. Wright, *THE METHODS OF PETROGRAPHIC-MICROSCOPE RESEARCH*, p. 148, (1911).

¹⁹ *Tschermak's Min. petr. Mittheil.*, 14, 563 (1894); 16, 180 (1896).

or five diameters over the size of the image observed directly with the conoscope. With long exposures the photographs are more distinct than the figures observed with the eye. Some of the photographs in Figures 5 and 5a were taken with exposures of fifteen minutes.

The values for the optic angles calculated by this method were the observed angles in oil and must be converted to 2E, the observed angle in air by multiplying the sine of the angle in oil by the index of refraction of the oil used in the bath. Paraffine oil was used because of its chemical inactivity and its high boiling point. The index of refraction of paraffine oil decreases rapidly with an increase in temperature so its index was measured at higher temperatures.

DETERMINATION OF THE INDEX OF REFRACTION OF PARAFFINE OIL

The indices of refraction of paraffine oil for sodium light at different temperatures were determined by the method of minimum deviation. The oil was heated in a hollow glass prism which was mounted upon the stage of the goniometer in an asbestos board chamber which was heated by a resistance unit. A thermometer was immersed directly in the oil and its readings were corrected for stem emergence. Plotting the values of the index of refraction against the temperature gave the index as a straight line function of the temperature.

INDICES OF REFRACTION OF PARAFFINE OIL. (MINIMUM DEVIATION)

Temperature C.	Index of Refraction
27	1.4813
45	1.4766
62	1.4712
75.5	1.4666
93.8	1.4619
109	1.4570
119.2	1.4537
130	1.4517
152	1.4441
156.5	1.4436
186	1.4371
203	1.4277
206	1.4290
212	1.4278

METHODS OF PROCEDURE

With a gradual increase in temperature a crystal of heulandite will slowly dehydrate and rotate the plane of the optic axes. This dehydration will proceed progressively from the surface of the crystal to the center and will give a series of lamellae with slightly different orientations. However, if the temperature increase is too rapid this development of lamellae is very pronounced, the brushes of the interference figure will disappear, and give only the lemniscates of the interference figure as is shown in Figure 5a, L. The brushes of the interference figure are formed where the optical directions of the crystal are parallel to the vibration directions of the two nicols. If, then, because of the different orientations of the lamellae, the crystal is not optically homogeneous, the brushes will disappear. By regulating the rate of increase of temperature to a point where the brushes are always visible, uniform conditions will prevail in the crystal.

The preliminary observations in this investigation were wholly of a qualitative nature. A number of sections were made from different crystals and their optical properties were observed through the same temperature intervals by alternately raising and lowering the temperature. This gave a general knowledge of the behavior of the crystals at different temperatures. With this general knowledge of the crystals as a background, measurements of the optic plane and optic angle were made through the whole temperature range up to 300° C. Preliminary curves of the optical properties were plotted from these values. The final determinations were made upon the clearest and best developed crystals and photographs were taken at those points which the preliminary work had revealed as significant.

A crystal which has been dehydrated in oil can be restored to its original condition by dissolving the oil in alcohol and then boiling in water to remove the alcohol. One section was treated in this way twice and the same variation in optical properties was observed three successive times. Observations were also made through the short temperature intervals which can be obtained with water and alcohol baths. Heulandite is not attacked by concentrated sulphuric acid but it is rapidly dehydrated. These sections can also be restored to their original condition by boiling them in water.

GENERAL CHARACTERISTICS OF THE CURVES
OF OPTICAL PROPERTIES

The curve, obtained by plotting the rotation of the optic plane against the temperature, falls into two general sections. The first section of the curve covers the temperature interval between 25° - 177° C. through which the rotation is slow and uniform. The total rotation in this interval is 19° and when plotted with the temperature gives a perfectly straight line (Figure 2). The second section is characterized by a rapid rotation of the optic plane which reaches a maximum of 120° at a temperature of 320° C.

If we examine the curve obtained by plotting the size of the optic angle with the temperature, we find the same general division into two distinct phases (Figure 3). The first effect of increasing the temperature is to enlarge slightly the optic axial angle but this is followed by an abrupt and rapid decrease in the size of this angle which reaches a minimum at a temperature of 190° C. The second phase is characterized by a rapid increase in the optic angle. At 300° C. the optic axes have passed out of the field of vision and the optic angle has value of approximately 120° .

REVERSIBILITY OF THE CURVES OF THE OPTICAL PROPERTIES

Reversibility of the curves of the optical properties is only possible when a decrease in temperature is accompanied by rehydration. If a crystal of heulandite is partially dehydrated in air and then allowed to cool, it will slowly return to its original state of hydration by absorbing moisture from the air, but if it is heated in an oil bath this rehydration by the absorption of moisture is manifestly impossible. Hence, upon cooling to room temperature we may determine the optical constants of a partially dehydrated crystal under the same conditions under which we originally determined the optical constants of the hydrated crystal. Any changes observed upon reheating the crystal will be due to the variation in temperature alone, unless the heating is carried to a point where further dehydration will take place. Figure 4 is a graphical representation of the changes in the position of the optic plane and in the size of the optic angle, which accompany heating to definite temperature, cooling in oil to prevent rehydration, and then reheating to a still higher temperature.

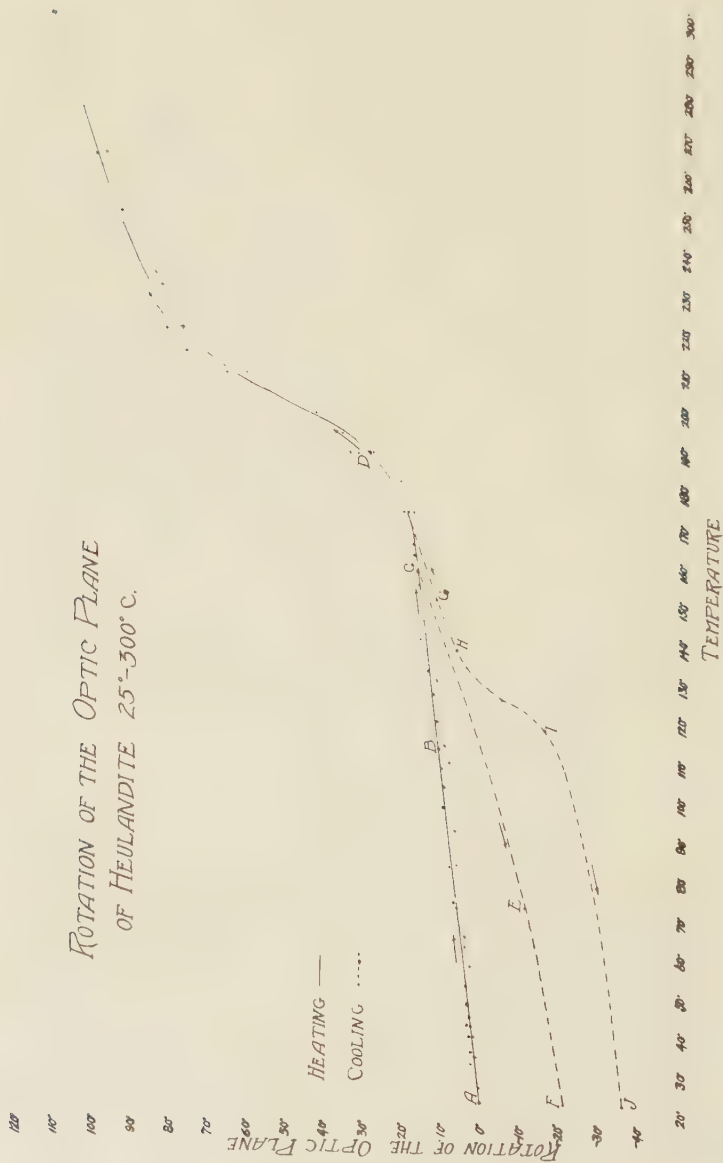
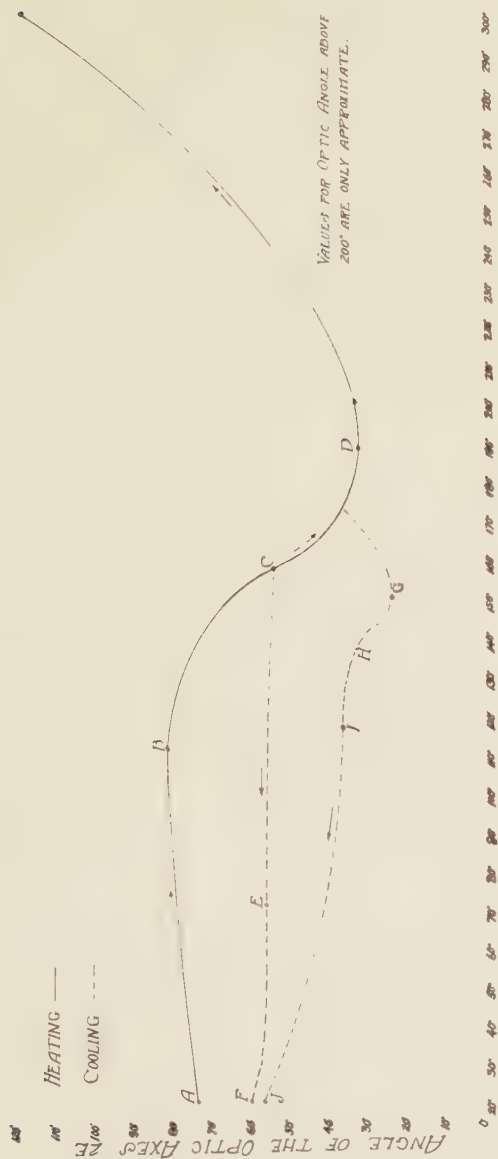


Fig 2.

VARIATION IN THE OPTIC ANGLE
OF HEULANDITE 25°-300° C.



TEMPERATURE

FIG. 3.

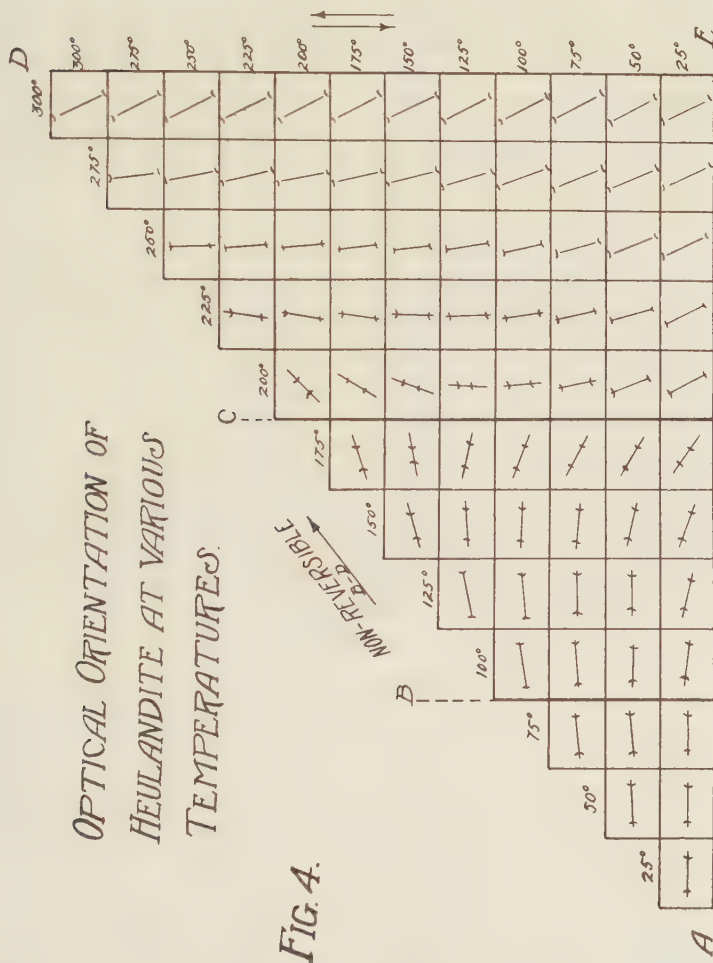
If we start at A, Figure 4, and pass along the diagonal ABCD, each step represents successive intervals of rising temperature. The change is progressive from 25° to 300° C. and shows a regular variation in the optical directions of the crystal. Each vertical column represents the variations in optical properties that will be found upon cooling the crystal from any definite temperature. For example, if we start at A and pass along the diagonal to the vertical column with the caption 125° , we shall observe that the plane of the optic axes has rotated counter-clockwise and that the angle of the optic axes is slightly larger. If the crystal is now allowed to cool, the optic plane will pass successively through the stages shown in the vertical column and become stationary in the position given at the base of the column. This then, is the position of the optic plane for a crystal which has been dehydrated at a temperature of 125° C. and allowed to cool to room temperature.

Upon reheating the crystal, the optic plane will pass through the successive stages in the reverse manner from that observed during the cooling, until, at 125° C. it will be in the position shown at the top of the column. With further heating the movement of the optic plane will be that shown along the diagonal. If the increase in temperature is carried to 175° C. and the crystal is again allowed to cool, the variations shown in the 175° column may be observed in the same manner as those observed in the 125° column.

The 25° temperature interval used in this diagram is an arbitrary unit. If a temperature interval of $12\frac{1}{2}^{\circ}$ were chosen it would show the intermediate stages between those given in Figure 4. The whole series of observations indicated in each column cannot be seen upon any one crystal because the alternate expansion and contraction gradually destroys the crystal and it becomes nearly opaque.

Through the temperature range 25° - 100° C., AB, Figure 4, the curve of the optical properties is completely reversible. This upper limit of reversibility is not a characteristic of the crystal itself, but rather of the conditions of the experiment, which allows rehydration to accompany cooling. If the crystal is heated to a temperature below 100° C. the water which is driven off will remain as a thin film between the crystal and the oil, and will be reabsorbed by the crystal upon cooling. The upper limit is not definitely located at 100° C. but may be reached at a somewhat lower temperature if the

crystal is held at that temperature for a considerable length of time. In one case where the temperature was held constant for three days at 85°C . the optic plane did not return to its original position upon cooling, but showed the behavior which is characteristic when the water is permanently lost to the crystal.



MEASUREMENT OF THE CHANGE IN DOUBLE REFRACTION

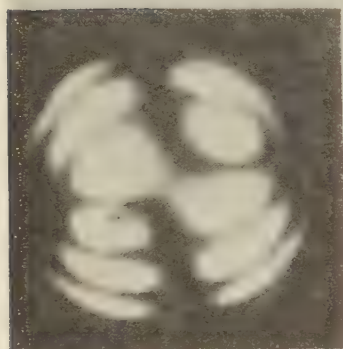
It has been previously noted that the double refraction of heulandite is very low. This double refraction can be measured with exactness only under ideal conditions, but once measured, it will furnish a basis by which comparative values for the double refraction at higher temperatures may be determined. In a biaxial interference figure, with crossed nicols, the lemniscate interference bands are formed where the phasal difference of converging monochromatic light is one wave length or a multiple of one wave length. The phasal difference of two rays of light emerging from the surface of a crystal is dependent upon the distance they have travelled through the crystal and upon the double refraction of the mineral. Therefore, upon the same section or upon sections of equal thickness, the double refraction is directly proportional to the number of interference bands surrounding the optic axes. The optic axes and the acute bisectrix are perpendicular, respectively, to vibration directions of β and α , so therefore, the number of rings between an optic axis and the acute bisectrix is proportional to the double refraction $\beta-\alpha$.

All of the photographs shown in Figures 5 and 5a were taken upon the same section which was 1.30 mm. thick, and when the interference figure was in the 45° position at 25° C. there were $3\frac{1}{2}$ interference bands between the optic axes and the acute bisectrix. The value of the double refraction $\beta-\alpha$ at this temperature is 0.0017, so each band represents an approximate double refraction of 0.0005. This method is only approximate because the fractions of an interference band must be estimated.

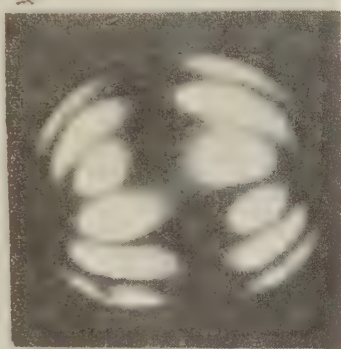
THE APPARENT UNIAXIALITY POINT

DesCloizeaux and Rinne have reported that heulandite became uniaxial at temperatures of 100° and 80° C., respectively. Their observations were made under the microscope and were purely of a descriptive nature. Under these conditions it would be very easy to give this interpretation to the facts observed during the rotation of the optic plane of a crystal whose optic angle was small.

This may be readily seen from the photographs G, H, I, and J, Figure 5a, which were taken at the successive temperatures of 154° , 141° , 121° , and 25° C., with the nicols horizontal and vertical. In G the optic plane is nearly horizontal and the brushes lie in the upper



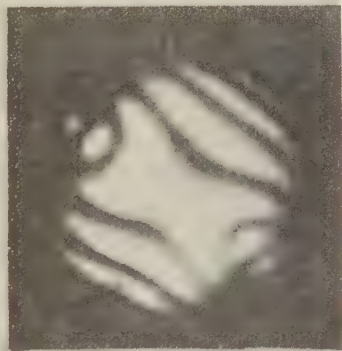
G



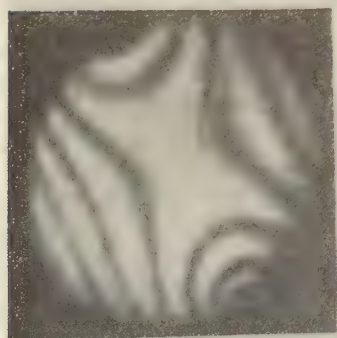
H



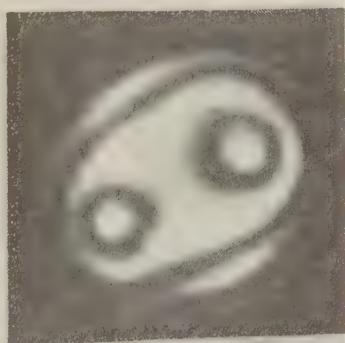
I



J



K



L

FIG. 5a.

right and the lower left quadrants. In H the optic plane has rotated slightly in a clockwise direction and the brushes have just begun to separate into the upper left and lower right quadrants. I and J show a further rotation of the optic plane and also an increase in the size of the optic angle. If the rotation of the optic plane is followed by rotating the nicols in such a manner that they are always at 45° with the optical directions of the crystal, the true biaxial nature of the crystal is always apparent. It can also be observed from the photographs that the interference bands surrounding the optic axes are always elliptical, while in the case of uniaxiality they should be circular.

For a more detailed description of the variations in the optical properties through the range of temperatures from 25° to 300° C., it is convenient to divide the temperature range into four intervals, 25 - 100° , 100 - 177° , 177 - 192° , and 192 - 300° C. In all cases where variations in the size of the optic angle are given, the numerical values refer to $2E$, the apparent angle in air, although in most cases these values have been calculated from the observed angle in oil.

OPTICAL CHANGES IN THE INTERVAL 25° - 100° C.

The optical changes in this interval are not very great and equilibrium is reached in a relatively short period of time. If a crystal is rapidly heated and then held at a constant temperature the rotation reaches a maximum in five to ten minutes and will remain indefinitely at that point. To verify this observation, crystals were held at constant temperatures of 32° , 50° , and 67° for two days without experiencing any further rotation than that observed shortly after they reached that temperature.

The total rotation through this temperature interval is $9\frac{1}{2}^\circ$ and the angle of the optic axes increases 7° . There is no appreciable change in the double refraction. A number of sections were heated in water to a temperature of 95° C. and a rotation of $6\frac{1}{2}^\circ$ was observed. This rotation was in the same direction as that observed in oil. The maximum rotation in an alcohol bath was $5\frac{1}{2}^\circ$ at a temperature of 74° C.

OPTICAL CHANGES IN THE INTERVAL 100° - 177° C.

The rotation of the optic plane through this temperature interval is of the same character as that observed in heating the crystals up

to a temperature of 100° C. The curve obtained by plotting the rotation with the temperature is a continuation of the straight line established in the previous interval. The optic angle shows a slight increase in size and reaches a maximum at about 115° C. when it begins to diminish rapidly. The most marked change is observed in the enlargement of the lemniscate interference bands due to the decrease in the double refraction. This is readily observed in the photographs B and C (Figure 5). In B there has been no perceptible change from the number of rings in A which shows the same crystal at room temperature, but the change in C is very pronounced. Here only $1\frac{1}{2}$ bands lie between the optic axes and the acute bisectrix while in the original photograph A there were $3\frac{1}{2}$ bands, which shows that the double refraction is less than one-half of the original value.

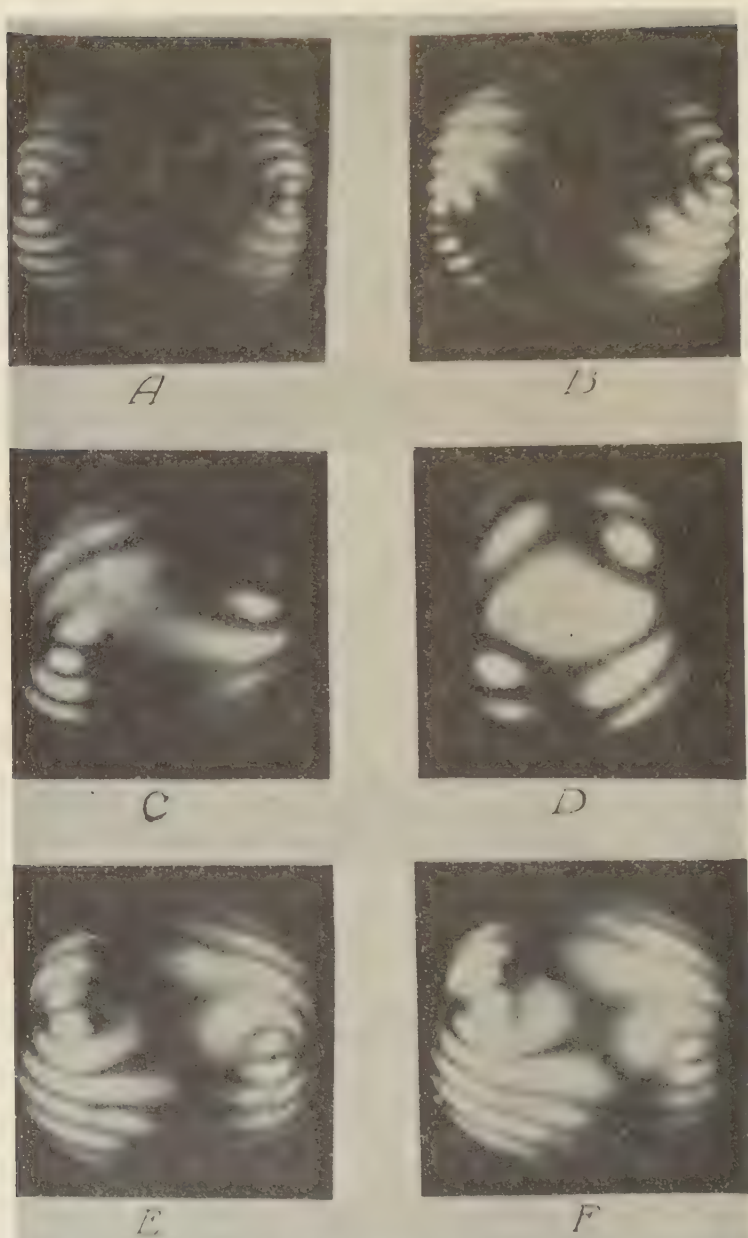
In Figures 2 and 3, two cooling curves are drawn which correspond to the similarly lettered photographs in Figures 5 and 5a. CEF shows the effect of cooling from a temperature of 161° C. to 25° C. There is a very pronounced rotation of the optical plane but practically no change in the size of the optic angle. The double refraction increases slightly between C and E, but remains fairly constant between E and F. These three photographs follow closely the changes depicted graphically in Figure 4, 150° vertical column.

More striking changes are shown by the cooling curve GHIJ and the corresponding photographs, although for this curve the crystal was heated to a temperature only 16° higher than for the curve CEF. In G, H, and I, there are no interference bands between the optic axes and the acute bisectrix, and the double refraction is therefore less than one-fourth of the double refraction shown in the photograph A. The angle of the optic axes in G is 24° , while the original value was 74° .

A comparison of the photographs A, F, and J taken at 25° C., but in different stages of hydration, shows:

	Rotation	Optic Angle	Double Refraction
A	—	74°	0.0017
F	21°	61°	0.0010
J	36°	57°	0.0008

These changes are produced by heating a crystal to different temperatures and then cooling, and are therefore changes due to

*FIG. 5.*

dehydration alone. The more striking changes observed at higher temperatures are due both to dehydration and to temperature effects. These resultant changes in the optical properties are more readily observed in Figure 4, A to E, where they are graphically illustrated.

OPTICAL CHANGES IN THE INTERVAL 177°-192° C.

The transition point between the gradual and uniform rotation of the optic plane and the more rapid rotation at higher temperatures lies in this temperature interval. Weigel places the transition point at 180° C. while Scheuman places it at 186° C. A study of the optical properties also shows that a definite structural change is taking place. Observations which were easily made at lower temperatures become very difficult due to anomalous conditions which develop in the interference figures. Such interference figures as the one shown in the photograph L Figure 5a, become very characteristic.

The lamellar structure in which some of the lamellae have different orientations from the others is revealed in the absence of brushes. A difference in double refraction around the two optic axes is shown by a variation in the distance between the interference bands surrounding the axes. The anomalous character of this interference figure is not so pronounced as in most of the cases when the changes were so rapid that it was impossible to photograph them. This photograph was taken with a twelve minute exposure and a movement of the figure during the exposure is shown by the blurring of the bands.

At higher temperatures the conditions become more stable and it is possible to obtain photographs of normal interference figures such as D, Figure 5, which was taken at a temperature of 192° C.

A distinct difference in the character of the changes produced upon cooling is to be observed above and below this temperature interval. This may be clearly seen from the graphic representation of these changes in Figure 4. Below this temperature cooling is accompanied by a reverse rotation of the optic plane through its original position, while above the temperature the rotation upon cooling is in the same direction as that observed when heating the crystals.

OPTICAL CHANGES IN THE INTERVAL 192°-300° C

The difficulties of accurate observation increase rapidly as we pass to these higher temperatures. In the first part of this region, up to 250° C., the interference figures are clear and distinct, but the double refraction is so low that only a few of the lemniscate interference bands are visible. Above 250° C. observations can only be of a qualitative nature, because the optic axes soon pass out of the field of vision and any changes in the optical properties can be followed only by the movements of the few interference bands that remain visible. To these inherent difficulties are added the experimental difficulties of working at these temperatures.

At 300° C. the paraffine oil volatilizes rapidly and decomposition soon gives it a yellowish tint. Many of the poorer sections become opaque before this temperature is reached, because of the formation of a large number of small cracks through the crystal. These conditions tend to materially reduce the intensity of the light and the interference figures become hazy and indistinct. To take photographs of the interference figures, it is necessary to keep the lens systems in direct contact with the glass windows of the oil bath for twelve or fifteen minutes, so no photographs were taken above 192° C. because of the danger of cracking the lenses and of melting the canada balsam between the two sections of the nicol prism.

The changes which take place in the optical properties through this temperature interval may best be followed by referring to Figure 4, which shows the orientation of the optic plane and the size of the optic angle at different temperatures. From the photograph D, Figure 5, it may be seen that the double refraction is very low because there are no interference bands formed between the two optic axes. As the temperature increases, the size of the optic angle increases greatly but the double refraction still remains low.

Cooling from a temperature of 192° to 25° C. brings the optic plane into the position shown in photograph K, Figure 5a, in which the optic axes lie just outside the field of vision. If the crystals are heated to a higher temperature, the optic axes move still further outside of the field and none of the circular interference bands surrounding the optic axes are visible. Upon cooling from a temperature greater than 192° the plane of the optic axes always returns to the same position but the size of the optic angle changes slightly (Fig. 4).

The final stage is reached in the vicinity of 300° C. in which the position of the optic plane and the size of the optic angle do not vary upon heating and cooling. At this point the optic angle is greater than 90° ; therefore, it is the obtuse bisectrix which is now perpendicular to the cleavage face (010).

DEHYDRATION AT CONSTANT TEMPERATURE

The resultant changes in the position of the optic plane and in the size of the optic angle, which are produced by heating to a definite temperature and allowing the crystals to cool in oil, are shown in Figure 4, A. to E. These changes are produced by dehydration and not by the influence of temperature; therefore it should be possible to duplicate these changes by dehydration with sulphuric acid. This was found to be the case.

If the crystals are placed in a desiccator over sulphuric acid they slowly dehydrate and an observable change in the position of the optic plane is produced in twenty-four hours. This method is very slow and the crystals become cloudy but their optical properties can be observed if they are immersed in oil. Heulandite is soluble in dilute acids but it is not attacked by concentrated sulphuric acid, so some of the crystals were placed in a small sulphuric acid bath and mounted between the polarizer and the analyzer. The strength of the acid was maintained by frequently removing it and replacing it with fresh acid.

Dehydration is comparatively rapid when the crystals are immersed directly in the acid and a noticeable change in the position of the optic plane takes place in fifteen minutes. The dehydration starts at the surface of the crystal and proceeds progressively inward with a consequent distortion of the interference figure, due to the fact that the crystal develops lamellae of different compositions. These anomalous figures are similar to those which develop when a crystal is rapidly heated in oil. Equilibrium is reached in two to three days and the resulting interference figure is similar to the photograph K, Figure 5a, except that the optic axes lie a trifle further outside the field of vision. The final rotation of the optic plane is the same as that produced by heating, although the increase in the size of the optic angle is not quite so pronounced. This indicates that the dehydration by the sulphuric acid was not quite so complete as that produced by heating.

This process of dehydration may be reversed by slowly diluting the acid. The addition of water to the sulphuric acid increases the vapor pressure of the acid and causes rehydration of the crystal. This rehydration can be carried to a point where the interference figure is similar to that shown in photograph J, Figure 5a. With further dilution of the acid the crystal rapidly disintegrates, due to the solvent effect of the dilute acid.

One crystal was mounted in a bath of absolute alcohol but no noticeable change was produced in twenty-four hours.

ROTATION OF THE OPTIC PLANE
(Values plotted in Figure 2)

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
42° C.	2°	37° C.	2°	35° C.	2°15'
60	3	45	2 30'	38	2 15
65	4	47	3	42	3
67½	4 30'	55	4	45	3 30
85½	6 15	75	6 15	50	3 30
94½	7	105½	9 45	85	8
112	8 30	122½	12	100½	10
116½	10	129½	13	110½	10 30
133	12	158	17	135½	14 30
158	15 30	165½	18	144	16 30
177	18 30	177	20	163	19
185	22	192	33	177	21
192	27			192	35
202	44			212	67
212	62			218	73
224	79			223½	83
235	84			254	95
238	86			269	102
269	99				

ROTATION OF THE OPTIC PLANE UPON COOLING

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
85°	7°	110°	10°	120°	12°
72	3	92	5	102	5½
67	0	75	0	85	0
50	-1	64	-3	61	-6
45	-3	40	-7	40	-10
39	-4	25	-8	25	-11
25	-4				

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
137°	15°	150°	16°	161°	17°
105	1	130	9	121	3
50	-12	99	-2	75	-11
25	-14	83	-6	25	-21
		60	-12		
		41	-16		
		25	-18		

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
177°	20°	195°	36°	210°	59°
154	12½	160	58	200	63
141	7	139	67	155	80
121	-16	92	95	108	96
80	-22	60	106	85	104
25	-35	25	115	50	106
				25	112

Temp.	Rotation	Temp.	Rotation	Temp.	Rotation
229°	85°	260°	93°	300°	110°
186	87	200	94	100	113
160	87	130	98	25	112
130	94	110	103		
100	103	70	106		
50	110	25	117		
25	116				

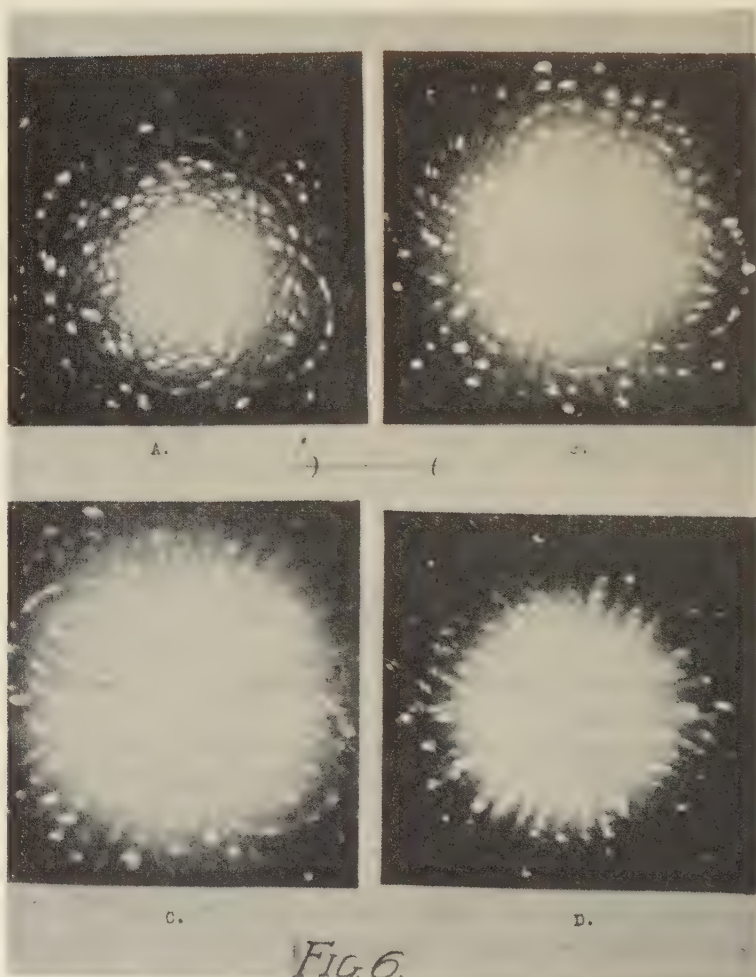
STRUCTURAL CHANGES

No determinations of the lattice structure of the complex silicates have been made but Laue diagrams have been used to reveal the structural similarity of the silicates. Rinne²⁰ has also used the Laue diagrams to show the changes in symmetry which accompany dehydration of crystals and he gives diagrams of heulandite and meta-heulandite.

The photographs in Figure 6 were made upon the same crystals that were used for the determination of the optical properties, by allowing the X-rays to strike perpendicularly upon cleavage sections parallel to (010). A is the Laue diagram of the normal heulandite at 25 ° C. B was taken upon the same section after it had been heated at 300° C. for three minutes and allowed to cool in oil to room temperature. It shows no change in symmetry although the

²⁰ CRYSTALS AND THE FINE STRUCTURE OF MATTER, p. 146, (1924).

dehydration of the crystal has shifted the position of the optic plane from the horizontal until it is perpendicular to the two larger circles of the diagram. C was taken upon a section which had been heated at 210° C. for two hours and shows a slight breaking down of the structure though the main structural outlines still persist. In the photograph D we may see the decided change that has taken



place in a crystal section which had been dehydrated in oil at 300° C two months previous to the time when the photograph was taken. This reproduction does not reveal the traces of the original structure as well as the negative, but the sunburst effect is characteristic of Laue diagrams of a heterogeneous mixture of minute crystals.

These diagrams indicate that meta-heulandite (Rinne) is a semi-permanent condition whose existence is dependent upon the stability of the silicate structure after the removal of the water. The gradual breaking down of this structure is revealed in the photograph D, Figure 6, which was taken two months after dehydration. Its similarity to the original structure is shown by B, Figure 6, taken immediately after dehydration. The structural significance of water in the silicates cannot be determined from X-ray studies because of the masking influence of the heavier elements.

DISCUSSION

From a consideration of the fact that the optical properties of heulandite bear a direct relationship to the amount of water present, we must conclude that the water is not extraneous, but plays a definite role in the structure of the crystals. If the water were present, not in any definite structural relationship but as an isotropic medium, its removal would have but slight effect upon the optical properties. If the water were present in its natural isotropic state and then were completely replaced by another isotropic substance (e.g., paraffine oil), the relative change in the double refraction would be about 1 per cent and would produce but a slight change in the interference figures. Such a hypotheses, then cannot account for the marked change that is observed when heulandite is dehydrated, and we must attribute this change to a structural alteration which is contingent upon the loss of water.

In dealing with the hydrated silicates, conditions are considerably different from those found in the typical hydrated salts. The amount of water present is much less and the tenacity of the crystal structure is much greater than in the hydrated salts. This is clearly shown in the following table. The values in the third column, the percentages of water by volume, are calculated from the first and second columns on the assumption (made for statistical comparison only) that the water of the hydrate has a density of one.

	per cent H ₂ O(weight)	Sp. Gr.	per cent H ₂ O(volume)	Hardness
Na ₂ SO ₄ .10H ₂ O	55.9	1.48	82.7	1.5
MgSO ₄ .7H ₂ O	51.2	1.70	87.0	2.0
FeSO ₄ .7H ₂ O	45.3	1.89	85.6	2.0
CuSO ₄ .5H ₂ O	36.1	2.20	79.4	2.5
Heulandite	15.6	2.2	34.3	3.5-4.0
Chabazite	21.3	2.1	44.73	4.0-5.0
Apophyllite	16.1	2.3	37.03	4.5-5.0

In the hydrated salts the greater part of the crystal is water, and therefore, the crystal form would be dependent to a great extent upon the H₂O molecule. The loss of this water would necessarily destroy the crystal form. On the other hand, in the hydrated silicates, water plays a minor rôle and the crystal form would be determined by the silicate molecule. This hypothesis may account for the stability of the crystal form of zeolites after losing the water of crystallization. Added evidence of the stability of the crystal structure of the two types of hydrates may be found in the comparative hardness. Mohs's scale of hardness is only a relative standard but determinations of absolute difference in hardness between 2 and 4, as given in Mohs's, range as high as 1 to 20.

The existence of water in a definite structural relationship to the silicate molecule will account for the variations in the optical properties that have been observed in the crystals of heulandite. The gradual removal of this water, by heating slowly to 177° C. would produce a change in the fields of force surrounding the silicate molecule and consequently a change in the optical properties. Above a temperature of 177° C. the cumulative effect of these stresses would be so great that they would produce a rupture in the silicate structure which is revealed in both the optical changes and in the Laue diagrams. The final and complete breaking down of the crystalline structure is very slow and must be measured in periods of months duration.

SUMMARY

1. Water plays a definite role in the structure of heulandite.
2. Above a temperature of 177° C. the structure of heulandite exists in a metastable condition. This is the metaheulandite which Rinne has established from Laue diagrams, but its persistence is due to the stability of the silicate structure and will break down if given a long enough period of time. The development of this

metastable condition is correlated with the 3 molecule hydrate (Weigel and Scheuman).

3. The optical variations shown in Figure 4, A to E, are due to dehydration alone while the more pronounced changes are due to temperature effects.

4. The crystals always remain biaxial and positive. The apparent uniaxiality is due to the rotation of the optic plane when the angle of the optic axes is small.

5. During all the changes observed, the bisectrix remains parallel to the *b* axis, which indicates that the crystals are monoclinic.

NOTES AND NEWS

A PROBABLE OCCURRENCE OF NATIVE LEAD NEAR
PORTLAND, MAINEGERALD R. MACCARTHY, *Chapel Hill, North Carolina*

In the summer of 1920 the writer obtained several specimens of metallic lead which occurred as a discontinuous sheet projecting from the joints of a gneissic cliff at Cape Elizabeth, near Portland, Maine. At the time the importance of a discovery of native lead was not realized, and little attention other than the prying out of several small specimens was paid to it. Since then no opportunity for a second visit has presented itself, but hoping that some one may find the time to look it up, the following facts are offered.

The lead was found in two or more vertical joints in a gneissic cliff, near the extremity, and on the shoreward side of a rock spit running northward a few hundred feet north of the Cape Elizabeth Casino. The metal, which seemed to be of natural origin, was in the form of thin sheets, about 4 or 5 mm. in thickness, and could be traced as a somewhat discontinuous streak for ten or fifteen feet along each of the joints in which it was found.

No chemical tests other than simple blowpiping were made, but the lead would seem to contain a little silver and perhaps some antimony. Its distribution along several vertical joints spaced rather far apart would seem to preclude the possibility of the overturning of a pot of molten metal on top of the low cliff, or of the lead being a relic of an abandoned rifle range, though a closer investigation might possibly indicate something of the kind. At any rate, the time spent in a more careful examination would be well worth while, should any mineral enthusiast chance to pass that way.

Mme. Curie, on June 7, laid the corner stone of a radium institute and hospital in Warsaw to be named in her honor.

Dr. H. Foster Bain, since 1921 director of the Bureau of Mines, has resigned. He has been appointed chief secretary of the American Institute of Mining and Metallurgical Engineers.

Mr. Henry R. Goodnow, 98 Riverside Drive, New York City, a member of the Mineralogical Society of America, died on May 3.

The report of the Committee on the Measurement of Geological Time by Atomic Disintegration states that the ratio of lead to uranium increases in the older uraniferous minerals. If lead from other sources can be eliminated the relative age of different minerals can be estimated.

For Tertiary minerals, Colorado pitchblende, carnotite, brannerite, tyuyamunite, betafite, etc., the ratio is less than .01. For those associated with the Appalachian uplift, whether in Connecticut, Saxony, or Cornwall, it is .04. For great pre-Devonian disturbances, especially south of the equator, it is .08, and for

various pre-Cambrian minerals, over .10, being for most of the pitchblendes that have been most closely studied .16, plus or minus .015.

The committee consists of Alfred C. Lane, chairman; H. V. Ellsworth, Frank L. Hess, S. C. Lind, R. B. Moore, and Roger C. Wells. The names of T. W. Richards and F. F. Grout have been recommended to be added to the committee.

Dr. Wheeler P. Davey, of the research laboratory of the General Electric Company, delivered a series of lectures on "X-ray Analysis of Crystal Structure" at the summer session of the graduate school in the physics department of the University of Michigan.

By making use of spectra obtained by passing X-rays through concentrated solutions of platinum ores and of the minerals gadolinite and columbite, Dr. Walter Noddack and his assistants, Otto Berg and Ida Tacke, discovered the missing chemical elements numbers 43 and 75. These elements fall in the group with manganese in the periodic table. Dr. Noddack has named them *masurium* and *rhenum*, after the territories lost by Germany as a result of the peace treaty.

Donald H. McLaughlin, chief geologist of the Cerro del Pasco Mining Corporation, in Peru, has been called to the professorship of mining engineering at Harvard University.

NEW MINERALS: NEW SPECIES

CLASS: NATIVE ELEMENTS.

"Palladium Amalgam"

J. B. HARRISON AND C. L. C. BOURNE. *The Official Gazette, British Guiana*, No. 71, (1925); Also No. 181, (1924).

NAME None given.

CHEMICAL PROPERTIES: A mercury amalgam of palladium. Formula: (Pd, Hg). Analysis: Pd 34.8–45.6, Hg 65.2–54.4. Upon heating it loses mercury leaving the palladium as a spongy mass.

PHYSICAL PROPERTIES: Malleable but somewhat brittle. Color white. Luster metallic. Sp. Gr. variable; with 64% Hg, 15.82; with 54% Hg, 13.48.

OCCURRENCE: Found in the diamond gravels of the Potaro River in the Kangeruma District, British Guiana, associated with gold.

DISCUSSION: The allopalladium from British Guiana described by L. J. Spencer (*Mineralog. Mag.*, 20, 217, 1924) came from the same source as the material here described and is believed by the above writers to be the same mineral as theirs. Dr. Spencer's material was apparently too scanty for detailed investigation. Artificial amalgams of palladium are well known but this is the first reported occurrence in nature.

W. F. FOSHAG

CLASS: SULFIDES, ETC. DIVISION: $R_2S : RS : R_2S = 1 : 2 : 2$.

Benjaminite

EARL V. SHANNON: Benjaminite, a new sulphosalt mineral of the klaprotholite group. *Proc. U. S. Nat. Mus.* **65**, 1, (1924).

NAME: In honor of Dr. Marcus *Benjamin*, of the United States National Museum.

CHEMICAL PROPERTIES: An argentiferous sulphobismuthite of lead and copper, $(Cu, Ag)_2S \cdot 2PbS \cdot 2Bi_2S_3$. Analysis (average of four analyses): Sb 25.18, Cu 4.69, Ag 3.51, Bi 50.78, S 15.84. No effect with HCl, $FeCl_3$, $HgCl_2$ or KOH. With HNO_3 effervesces and blackens, fumes tarnish brown.

PHYSICAL AND OPTICAL PROPERTIES: Strongly anisotropic. $H=3.3-3.5$. Color on fresh fracture, gray but tarnishing. Luster metallic with greasy appearance. Good cleavage in one direction.

OCCURRENCE: Found with chalcopyrite, pyrite, covellite, muscovite, molybdenite, and fluorite in quartz at the Outlaw Mine, twelve miles north of Manhattan, Nevada.

DISCUSSION: The samples were critically examined for homogeneity and apparently represented one mineral. It is, therefore, a new mineral, but the exact composition is unknown as the individual analyses show some variation.

W. F. F.

CLASS: PHOSPHATES, ETC. SUB-CLASS: HYDROXY-PHOSPHATES

Dussertite

J. BARTHOUX: Description d'un mineral nouveau: la dussertite. (Description of a new mineral: dussertite.). *Compt. Rend.*, **180**, 299-301 (1925).

NAME: In honor of M. *Dussert*.

CHEMICAL PROPERTIES: A hydrous arsenate of lime and ferric iron. Formula: $3(Fe, Al)_2O_3 \cdot 6(Ca, Mg)O \cdot 2As_2O_5 \cdot 9H_2O$. Analysis: As_2O_5 31.90, Fe_2O_3 31.24, FeO 0.52, CaO 22.03, Al_2O_3 2.37, MgO 0.34, SO_3 1.08, Cl tr, H_2O 10.61; total 100.09. Soluble in dilute hydrochloric acid.

CRYSTALLOGRAPHIC PROPERTIES: Hexagonal or trigonal. Small crystals tabular to the base.

PHYSICAL AND OPTICAL PROPERTIES: Color, green; in thin section, greenish yellow. Index of refraction between 1.80 and 1.88. Birefringence about 0.012. Uniaxial, negative. Pleochroic in shades of greenish yellow. Sp. Gr. 3.75. $H=3.5$.

OCCURRENCE: Found as crusts on tabular or cavernous quartz at Djebel Debar, Northeast of Hammon Meskhoutine, Province of Constantine, Algeria.

DISCUSSION: The composition of dussertite can be expressed by the formula $Ca_3(AsO_4)_2 \cdot 3Fe(OH)_3$. This brings it near the chondrasenite group but differs from the members of that group by the presence of the iron in a higher state of oxidation and crystallographically by being hexagonal instead of monoclinic.

W. F. F.